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BUREAU OF ECONOMIC GEOLOGY AND TECHNOLOGY

DIVISION OF CHEMISTRY

ENGINE STORAGE

Engineering Boiler Waters: Their Chemical Composition, Use, and Treatment

By

W. T. READ, Chemist

With a Preface

By

E. P. SCHOCH, Head of the Division



Published by the University six times a month and entered as
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Boiler Waters: Their Chemical Composition, Use, and Treatment

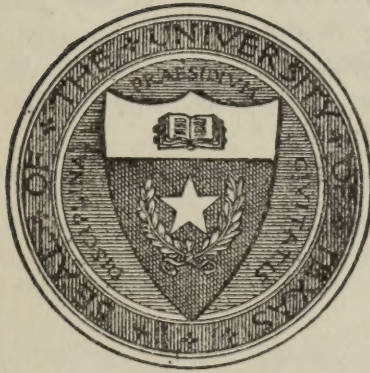
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The benefits of education and of useful knowledge, generally diffused through a community, are essential to the preservation of a free government.

Sam Houston

Cultivated mind is the guardian genius of democracy. . . . It is the only dictator that freemen acknowledge and the only security that freemen desire.

Mirabeau B. Lamar

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By W. T. Read

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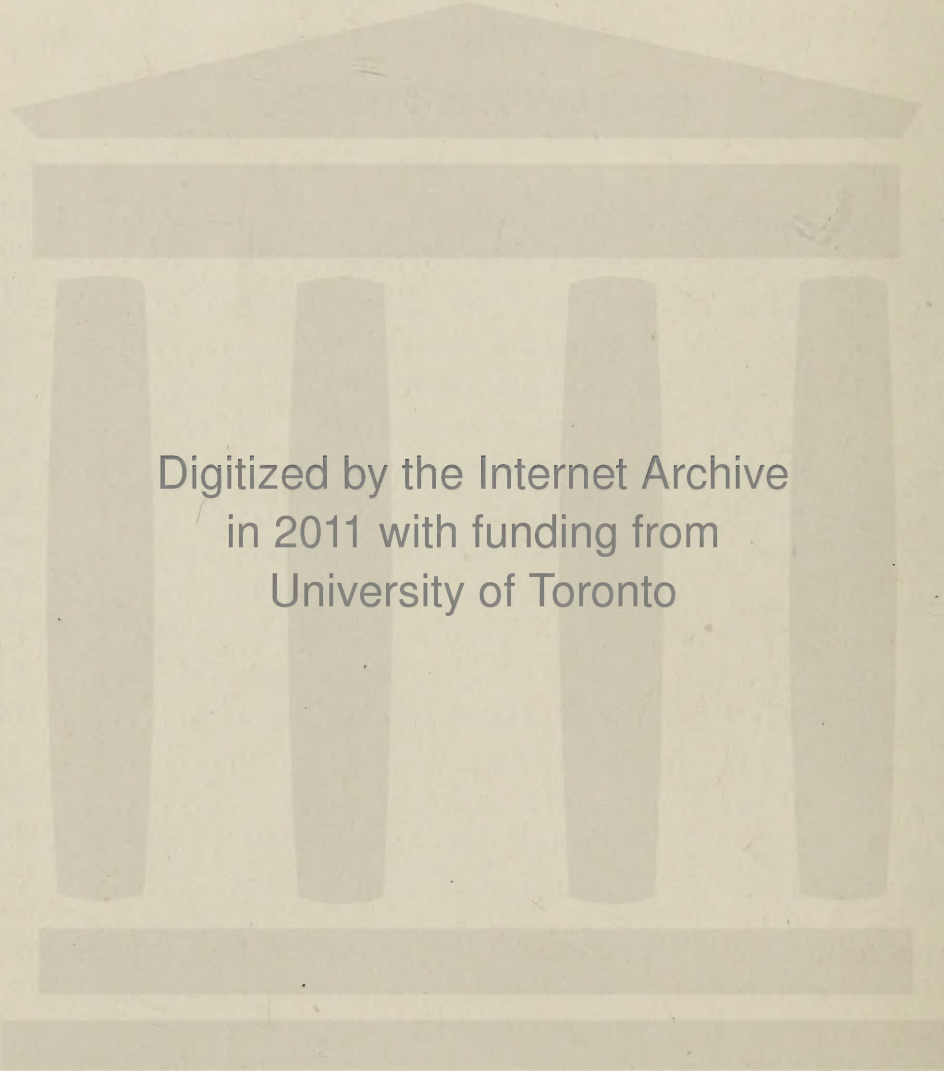
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PREFACE

AID ON WATER SOFTENING GIVEN BY THE UNIVERSITY OF TEXAS

BY E. P. SCHOCH

INTRODUCTION.—When in October, 1915, the University authorities established the Division of Chemistry of the Bureau of Economic Geology and Technology for the study of industrial problems of a chemical nature, it was realized at the outset that one of the most fundamental and most important chemical problems confronting industrials in this state is the softening of the water to be used in industrial plants. Very few steam boilers in Texas are supplied with softened water, and the use of hard water entails a great financial loss in fuel, in extra wear on the boilers and engines, and in money and time spent in removing scale. This state of affairs appeared to the writer to be a matter of public concern and well worth the making of a systematic campaign to urge steam users to soften their boiler water and to aid them in securing and operating a suitable apparatus.

PLAN OF PROCEDURE.—Anyone who operates or intends to install a steam boiler is asked to send, by prepaid express, about one gallon of the water used or to be used. The water should be sent in a clean glass bottle, but not in a jug. The bottle should be closed with a well-fitting stopper, and the latter secured by tying a cloth over it. A letter should be sent with it which gives the source of the water, the state of the boiler—that is, whether it is new or old, and, if old, whether or not trouble from scale formation, corrosion, or foaming has been experienced. After the water has been examined, the applicant will be advised what to do. If he puts in a softening apparatus, the Division of Chemistry stands ready to help him by keeping a chemical check on its operation, and if necessary, to send a man to inspect it. All of this is done free of charge except for the traveling expenses of an inspector sent out on request.

PURPOSE OF THIS BULLETIN.—The foregoing plan of operation has been followed for about a year. While we have reached comparatively few industrial plants during this time, yet we

are more convinced than ever of the public economy of proper boiler water softening; and in order to reach a larger number with less labor of correspondence, and to advise steam users more extensively on this question, we have issued the following Bulletin. It has been written by Mr. W. T. Read, who has had special charge of this work since June, 1916.

The Bulletin has been written to give all necessary information as to the causes of boiler troubles and the remedies for them. It is intended particularly for steam users who operate small plants, to educate them away from slipshod, wasteful, old-fashioned, careless, and dangerous methods of "letting things slide," pounding and chiselling at boiler scale, dosing boilers with any kind of a compound that a salesman may urge or suggest, worrying along with foaming boilers, and in general, wasting money, time, and labor. It has been written for the general reader who knows nothing about chemistry or the technical handling of a steam plant, and also for the technical man in actual charge of a plant who wants to have definite information for securing and operating the proper sort of a softening plant.

With this Bulletin, the Division of Chemistry intends to continue its plan of operation stated above and to make its campaign for boiler water softening not only more extensive, but more effective. We sincerely believe that the perusal of this Bulletin will convince many boiler operators of the economy of using softened waters and thus help us to reduce what is now a great national waste.

OTHER SERVICE RENDERED BY THE DIVISION OF CHEMISTRY.—This Division has been established for the purpose of giving Chemical aid in the recognition of development of Texas raw products, and to do experimental work in establishing or advancing industries using such raw products. At present, its investigations are concerned with the following materials: coal, lignite, petroleum, natural gas, graphite, paper pulp material, clay, cement and plaster material, water used for steam boilers and for irrigating, and other minerals of economic importance.

To aid in the exploration for the materials in Texas, the Division of Chemistry offers to examine free of charge, any sample

of these substances collected in such a manner as to secure a sample which is a fair representative of the material or which has a composition that is the average of all the different portions of the material represented by the sample. In addition to that, it is necessary that certain information be furnished concerning the material. Details concerning the sampling and the information to be supplied will be sent on request. The extent of the examination made will vary from a critical "looking at" or visual examination of the sample to a complete chemical analysis, as may be considered necessary and profitable by the staff of this Division.

Boiler Waters: Their Chemical Composition, Use and Treatment

BY W. T. READ

CHAPTER ONE

EFFECTS OF MINERALS IN WATER USED IN STEAM BOILERS

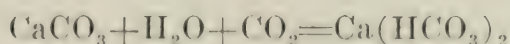
In general, all waters contain the same substances in solution in all sorts of amounts and proportions. Besides dissolved salts, most waters have certain gases in solution, most commonly carbon dioxide and air. This latter gas is usually spoken of as dissolved oxygen, since the nitrogen gas has no effect, and it is only the oxygen that causes trouble. There is also the special class of waters known as "sulphur waters." These contain hydrogen sulphide gas in solution. In addition to the dissolved minerals, most surface waters—especially Texas river waters in a wet season—carry a great deal of mud, fine clay, and vegetable matter in suspension. All of these have their part in causing boiler troubles. While the gases can be gotten rid of in open feed water heaters, and the mud settled and filtered out, the dissolved solids that cause scaling and corrosion cannot be eliminated or changed so that their harmful effects are neutralized *except by chemical treatment*. Hence before taking up the causes and remedies for boiler ailments, it is well to give a list of all the important salts that are commonly found in boiler waters, with some of their physical properties and chemical reactions.

1. *Common Salts in Boiler Water Supplies*

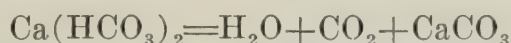
CALCIUM CARBONATE AND BICARBONATE

Marble, chalk and limestone, though different in physical structure, are mainly composed of the same substance, calcium carbonate, CaCO_3 . Water charged with carbon dioxide changes calcium carbonate to the more soluble bicarbonate, $\text{Ca}(\text{HCO}_3)_2$. Nearly all waters contain carbon dioxide, or carbonic acid gas, dissolved in them, because this gas, coming from decaying vegetable matter, from the smoke of all fires, and from all breathing animals, is readily dissolved by water. When water containing this gas comes in contact with limestone, it acts as an acid toward the calcium carbonate, and dissolves it extensively, forming cal-

cium bicarbonate or calcium acid carbonate, according to the equation:



As long as there is plenty of carbon dioxide in the water, this salt remains in solution, and the water remains clear. But if this gas is driven out of solution by boiling or simply by long standing, the reverse process begins, the acid carbonate of lime breaks down, giving up its carbon dioxide, and going back to the original carbonate of lime or calcium carbonate. Since the latter is not noticeably soluble in water, it separates from the solution as a white, crystalline, solid substance, the form of which depends on the conditions of the solution when the change takes place. The first change, that of solution, is the cause of most of the cutting away of the foundations of dams built on lime rock. The other change, that of precipitation from solution, is responsible for a good part of the scale formed when such water is boiled in any vessel ranging from the stove kettle in the kitchen to the big water tube boiler in the factory. The change is the reverse of that expressed by the chemical equation given above.



The carbon dioxide gas escapes, the acid carbonate is changed to the solid carbonate, and scale results.

MAGNESIUM CARBONATE AND BICARBONATE

In a general way what has been said about calcium carbonate and calcium bicarbonate may be said about magnesium carbonate and magnesium bicarbonate. A great many limestones contain magnesium carbonate. If the amount is considerable, the limestone is called a *dolomitic* limestone, and when the magnesium bicarbonate begins to approach an amount roughly equal to the calcium carbonate, the rock is called *dolomite*. Water charged with carbon dioxide dissolves magnesium carbonate in the same way as it dissolves calcium carbonate, but the magnesium carbonate, formed when this gas is gotten rid of, is much more soluble than the calcium carbonate produced under the same conditions. So in order to get rid of the magnesium before the water gets into the boiler, it has to be changed to the hydrate or hydroxide, which compound of magnesium is very soluble.

CALCIUM SULPHATE

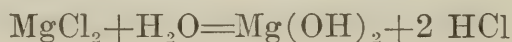
Chemical formula, CaSO_4 . This salt is familiar to every one in the form of gypsum. In this form it contains a definite amount of water in its crystals, which is called water of crystallization. When this water is partly driven out, plaster of Paris is formed, and the setting qualities of this substance are due to its taking up water again and forming interlacing crystals. Calcium sulphate is fairly soluble, water at ordinary temperatures being capable of carrying nearly 2400 parts per million (i. e. 2400 parts for every million parts of its water solution), or 140 grains per U. S. gallon. When the temperature of the solution rises above the boiling point of water under atmospheric pressure, calcium sulphate becomes appreciably less soluble. At 150°C . or 300°F . it will only go into solution to the extent of 500 to 700 parts per million (30 to 40 grains per U. S. gallon). As a water in steam boilers is concentrated under heavy pressure and at high temperature, any gypsum crystallizing out from it is deposited in the form of a *very hard, smooth* scale.

MAGNESIUM SULPHATE

Chemical formula, MgSO_4 . This is commonly known as "Epsom Salts." It is a very soluble white solid. If present alone in a boiler water, its only action would be to react with the water itself. This takes place only when the salt separates out on the boiler plates at the water edge. Magnesium sulphate at this point reacts with water to produce magnesium hydroxide and sulphuric acid. The magnesium hydroxide is very insoluble and forms a scale, and the sulphuric acid is very corrosive and will attack the material of the boiler. The chemical reaction is as follows:

**MAGNESIUM CHLORIDE**

Chemical formula, MgCl_2 . This is also a very soluble salt, the only action of which, when present alone, is to react with water at the water edge like magnesium sulphate according to this reaction:



Magnesium chloride reacts with water more readily and more extensively than the magnesium sulphate, and through the hydrochloric acid formed corrodes the iron of the boiler. Hence it is a particularly objectionable ingredient of boiler waters. This hydrochloric acid is a gas, and if the solution is concentrated enough, that is 1 per cent or more of the gas in the solution, it will distill out and corrode the boiler above the water line in the same way that the acid solution attacks it below the water line.

SODIUM CHLORIDE

Chemical formula, NaCl . This substance is what is known as "common salt." It is very soluble, and harmless with reference to scale production. As will be noted in the section on Corrosion, it simply furnishes the salt solution necessary to battery action, if the other conditions necessary for corrosion are present. If salt is allowed to accumulate by continual concentration of the boiler contents, and if suspended matter is present, foaming is likely to result.

SODIUM SULPHATE

Chemical formula, Na_2SO_4 . What has been said about sodium chloride applies equally well in describing the effect of sodium sulphate, with the exception that it is not as active in promoting battery action as the chloride—in other words, its solution is not as good a conductor of electricity as the solution of sodium chloride.

SODIUM CARBONATE

Chemical formula, Na_2CO_3 . This is familiarly known as "washing soda" or "soda ash." In waters containing considerable carbon dioxide, part of it is changed to sodium bicarbonate, NaHCO_3 . When a solution of sodium bicarbonate is boiled, it gives up carbon dioxide rather rapidly and finally passes entirely to sodium carbonate. Since this takes place readily, it is not necessary to consider the final effect of anything but the last named salt. This salt is very soluble. It is regarded as being more prone than any other of the sodium salts to cause foaming when in concentrated solutions. It also reacts with water to some extent to give caustic soda, or sodium hydroxide. This substance, when concentrated, is regarded as a source of danger

in leading to embrittlement of the steel and consequent cracking. As will be noted under the head of Corrosion, this is a much debated and still unsettled question.

SODIUM NITRATE

Chemical formula, NaNO_3 . This is commonly called "Chile saltpeter." Not many waters in Texas have any appreciable amounts of this salt, except some deep well waters in parts of North Texas, especially northwest from Mineral Wells. It is extremely soluble, and its only effect is probably that of aiding corrosion, because it gives up a part of its oxygen readily.

POTASSIUM SALTS

These are almost identical in their behavior with sodium salts, and for all practical purposes, the alkali metals, sodium and potassium, may be determined and reported together as sodium. Analyses of a large number of Texas waters have been made, and these waters found to contain an average of ten to fifteen times as much sodium as potassium. Hence the error in considering everything under the single head of sodium is not a great one.

2. *What an Analysis Means and What It Does Not Mean.*

IONS

In order to gain a clear idea of the meaning of a chemical analysis of water, it is necessary to outline in a general way the most recent and generally accepted theories as to the form which mineral matter has in solution. It is not to be expected that one who has never studied chemistry can understand the theory thoroughly, but any one can at least get an idea of the general principles involved. For the past twenty years the "Ion Theory" has been regarded by chemists as being so thoroughly borne out by actual facts that it has been made the basis of all analytical chemistry. Stated in the simplest possible terms, the general idea of this ion theory is this. When a soluble salt goes into solution, it is no longer electrically neutral, but breaks up into two (or more) parts called *ions*, one (or more) of which is positively charged, the other (or others) negatively charged. For instance: when the chloride of sodium, or common salt, is dissolved in water, it breaks up into sodium

(+)ions, each carrying one unit of *positive* electrical charge, and chloride(—)ions, each carrying one unit of *negative* electrical charge. These ions are constantly moving about and colliding with each other. If one sodium(+)ion meets another sodium(+)ion, both being positively charged, they repel each other. In the same way if one chloride(—)ion meets another chloride(—)ion, both being negatively charged, they will also repel each other. The only other possibility is the meeting of a sodium(+)ion with a chloride(—)ion. There is an attraction and combination to form sodium chloride, but only for an instant. Because of the force or tendency in the water to produce ions, they break apart once more. Suppose the water is gotten rid of by evaporation. The ions combine gradually as the amount of the water grows less, and its total ionizing power diminishes, until when all of the water is gone, solid sodium chloride is left in exactly the same form in which it was before.

ION COMBINATIONS

Suppose some potassium nitrate were added to this salt solution. Like the sodium chloride, most of it breaks up into these two ions, namely: positively charged potassium(+)ion and negatively charged nitrate(—)ion. Now this solution contains the ingredients for making four different combinations: sodium chloride, potassium chloride, sodium nitrate, and potassium nitrate. Not a single one of these four salts is present in the water as an individual salt, but the solution contains four kinds of ions: sodium(+), potassium(+), chloride(—) and nitrate(—). Under special conditions, such as evaporation, the first salt which reaches its limits of solubility—which depends upon both its quantity and its solubility—will be formed first in solid form regardless of whether it was originally present or not.

If a third salt, say magnesium sulphate is added, we have the necessary ingredients for making the following nine different salts from the six ions present: sodium chloride, sodium nitrate, sodium sulphate, potassium chloride, potassium nitrate, potassium sulphate, magnesium chloride, magnesium nitrate, magnesium sulphate. With a solution containing these six kinds of ions, it would be absolutely impossible to find out which three of the possible nine salts were originally put into solution. The pos-

sible formation of nine different salts is shown in the following diagram.

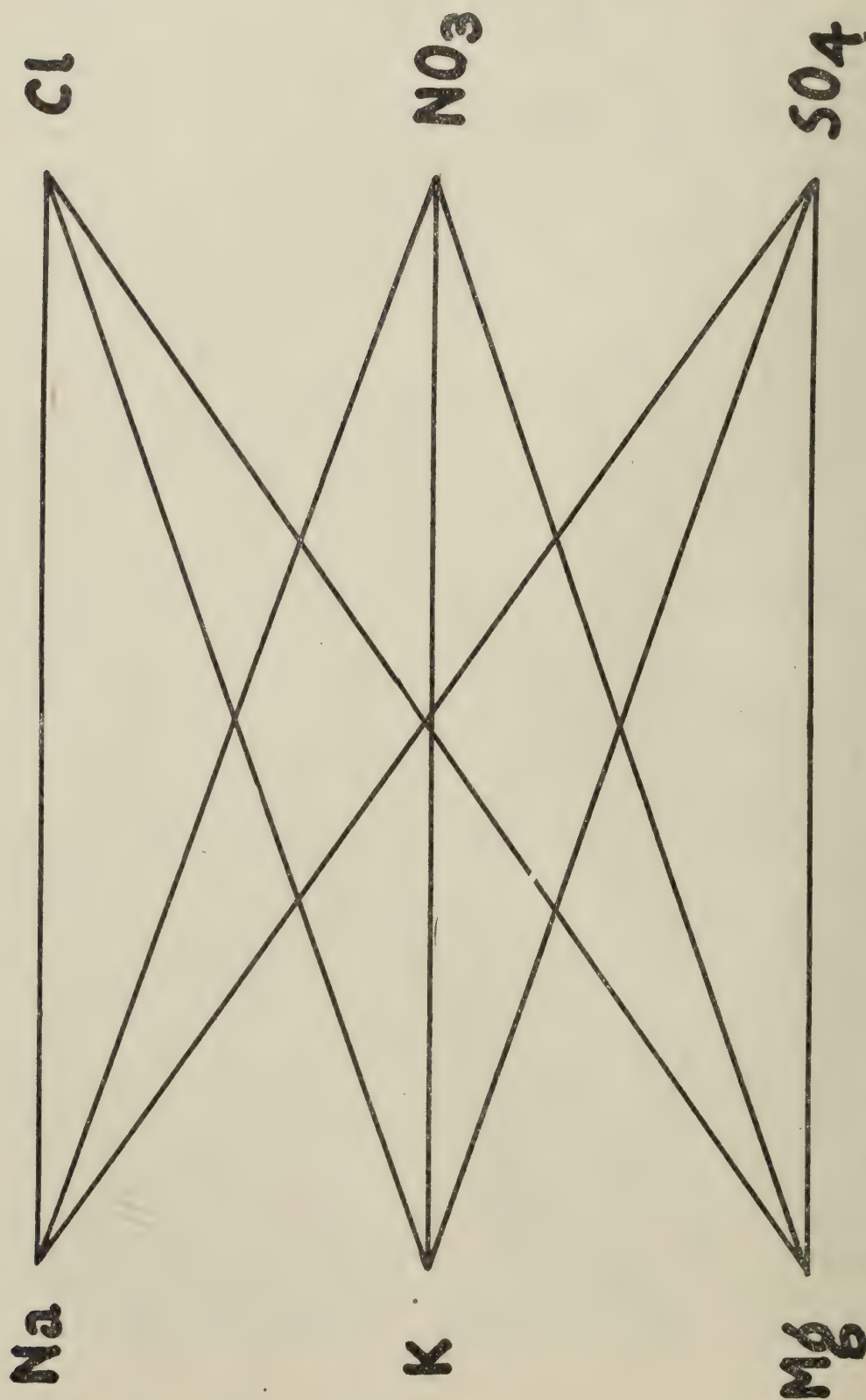


Fig. 1. Possible combination of three positive and three negative ions to form nine salts.

REPORT BY IONS

All the properties of a solution are due to the ions in solution. They each behave like individual substances. Ions are the only things a chemist determines when he makes an analysis. He identifies each ion by certain tests, and finds out accurately how much of each one is present. The only logical way to report a water is by ions, since nothing but ions are determined or can be determined in a water. This is the method employed by the United States Geological Survey, and is the only one used in this bulletin. It is not only just as easy, but it is much more accurate to calculate the scaling, corroding, and foaming tendencies of a water from the ions than from any "hypothetical combinations" that might be devised.

The following ions of soluble salts are ordinarily found in ground and surface waters. After the name of each ion is given its chemical symbol, its equivalent weight, and the reciprocal of its equivalent weight, which is a factor frequently used by chemists in calculating water analyses.

Name of Ion	Symbol	Equivalent Weight	Reciprocal of
			Equivalent Weight as Factor for Calculations
Calcium	Ca++	20.04	.0499
Magnesium	Mg++	12.16	.0822
Sodium	Na+	23.00	.0435
Potassium	K+	39.10	.0256
Hydrogen	H+	1.01	.9920
Carbonate	CO ₃ —	30.00	.0333
Bicarbonate	HCO ₃ —	61.01	.0164
Sulphate	SO ₄ —	48.04	.0208
Chloride	Cl—	35.46	.0282
Nitrate	NO ₃ —	62.01	.0161

Besides the ions of soluble salts, water may contain iron, aluminum and silicon in colloidal solution as oxides; iron oxide, Fe₂O₃; alumina, Al₂O₃; and silica, SiO₂. These three substances do not enter into any combination in waters, and they are electrically neutral. They are collected and weighed as such—that is in this chemical form—and hence analyses should present, and usually do present the amounts of the three oxides which are in a definite amount of a water. The weight of the iron alone may be obtained by multiplying the weight of its oxide by .6995; the

weight of the aluminium is gotten by multiplying the weight of its oxide by .5303. Silica is present in practically all waters in small amount. Carbon dioxide gas, or carbonic acid gas (CO_2) is also often present dissolved in the water, and is constantly evolved from waters containing the acid carbonates or bicarbonates as these break up to form carbonates. Hydrogen sulphide gas (H_2S) is found in so-called sulphur waters. It escapes if exposed to the air. Acids which form the hydrogen ion extensively are rarely present in Texas waters. When such an acid is present, the water has a sour taste, and thus the acidity can be easily detected. In the course of more than a thousand analyses of water made in the University of Texas laboratories, only three waters were found which were sour, and these were from a sand-clay formation in which there was no limestone. If limestone had been present, the acid would have been neutralized.

EQUIVALENTS

The analyses of waters usually present simply the number of parts per million of each ion present; but it is advisable to add a second number, which has the following significance. When multiplied by 60.62 times 10 raised to the 22nd power, or 60, 620,000,000,000,000,000,000, which is known as the "Avogadro Number", it gives the "number of individual combining portions" of that particular ion present in 1000 litres, which individual combining portion is of such weight that it will combine one to one with the corresponding portion of any other ion of opposite chemical nature. Thus one individual combining portion of a negative ion or acid radical is such an amount as will just combine with one individual combining portion of a positive ion or metal.

Nature requires that any definite amount of water must contain as many individual combining portions of negative ions as of positive ions. This is shown in the following figures, which give the composition of a water as actually found by analysis:

Positive Ions		Negative Ions	
Calcium ion...	$138 \times .0499 = 6.89$	Carbonate ion	$12 \times .0333 = 0.40$
Magnesium ion...	$29 \times .0822 = 2.38$	Bicarbonate ion	$290 \times .0164 = 4.76$
Sodium ion...	$69 \times .0434 = 2.99$	Sulphate ion	$198 \times .0208 = 4.12$
	—	Chloride ion...	$106 \times .0282 = 2.99$
Total of gram-equivalents		Total of gram-equivalents	
of positive ions.....	12.26	of negative ions.....	12.27

Hence the numbers referred to in the preceding paragraph are obtained by multiplying the amount of an ion actually determined by analysis in terms of parts per million by the reciprocal of its combining weight. This bears thus a fundamental relation to the absolute number of individual combining portions. The slight difference between the values of the sum of the numbers in the left column and the right column is due to undetermined traces of other ions, but these figures are sufficiently nearly equal to satisfy all practical purposes. These factors are employed to test the accuracy of an analysis and to determine the most probable source of error.

It is evident that these numbers so obtained in the foregoing calculations do not give the actual numbers of the individual combining portions of all the metal and acid ions, but that they must be multiplied by the Avogadro Number mentioned above in order to give the actual number of individual combining portions. Since we are here concerned merely with a comparison or relation of two such numbers, it is useless and unnecessarily troublesome to multiply them both by a constant value of such immense size as the Avogadro Number. For this reason we always use only the simpler numbers. These simple numbers are known as the number of *Gram-Equivalents* of any water constituent present in 1000 litres of the water.

CALCULATION OF SALTS FROM THE AMOUNT OF IONS

By means of these numbers it is very easy (though rarely necessary) to calculate the total amount of any one salt present in a water. For example, let us consider the question: "How much calcium carbonate (in parts per million) corresponds to the ions present in the water, the analysis of which is given above?" To answer this question, we proceed as follows:

Calcium carbonate is formed by a union of the calcium and of the carbonate ions. Since there is only 0.4 gram-equivalents per 1000 litres of the carbonate ion (which amounts to 12 parts per million), then only 0.4 gram-equivalents per 1000 litres of the calcium ion can be coupled with it to form calcium carbonate. Since 6.89 gram-equivalents per 1000 litres of calcium ion amount to 138 parts per million, 0.4 gram-equivalents amount to 0.4 divided by 6.89, multi-

40

plied by 138 or $\frac{0.4}{6.89}$ of 138, which equals 8 parts per million.

Hence in parts per million the total amount of calcium carbonate is $12+8=20$ parts per million. This illustrates how the amount of any salt may be figured out from the analytical report of ions as given in this publication.

If it is desired to find out how much calcium bicarbonate can be formed from the remaining calcium ions, continue the calculations as follows: It is evident that only 6.49 gram-equivalents of calcium ion are left to be considered ($6.89-0.4$). Since this is greater than the number of gram-equivalents of bicarbonate ion (4.76), it follows that the amount of this combined form is limited by the latter number, and only 4.76 gram-equivalents of the calcium ion can be coupled up with the bicarbonate ion. The number of parts per million of the bicarbonate ion is 290; that corresponding to 4.76

476

gram equivalents of calcium is $\frac{476}{689}$ of 138 or 95.3 parts per million

of calcium. Hence the total amount of calcium bicarbonate is $290+95.3$, or 385.3 parts per million. This second calculation shows how to calculate a combination of ions (or salt) with the provision that the ions forming a previously calculated combination are not available for the salt to be calculated. The process here given may be continued until all the ions are combined as salts.

Years ago, before it was known that the salts in very dilute solutions exist in the form of separate or free ions, the ions were arbitrarily assumed to be combined to form salts, and the reports stated the amounts of the combinations; but since there is absolutely no basis of fact that warrants the assumption that any particular combinations are formed rather than any other equally possible, and since no particularly useful purpose is served in representing the ions as being combined, this manner of reporting water analyses is now being gradually dispensed with, and has not been employed in this publication.

To illustrate how arbitrarily different chemists consider the ions to be combined, and how misleading this procedure is, we present here three different reports of the same water, for which the analytical results are given below. These three different reports are made on the basis of three different, but definitely used, assumptions concerning the combination of ions. All quantities in plain figures are in parts per million, while those in parentheses are in gram equivalents per 1,000 litres.

Name of Salt	Method 1		Method 2		Method 3	
Calcium Sulphate..	119	(1.75)	140	(2.06)	280	(4.11)
Calcium Carbonate.	20	(0.40)	None		20	(0.40)
Calcium Bicarbonate	385	(4.74)	387	(4.75)	195	(2.40)
Magnesium Sulphate	143	(2.38)	124	(2.06)	None	
Magnesium Chloride	None		17	(0.38)	None	
Magnesium Bicarbonate.....	None		None		172	(2.36)
Sodium Carbonate..	None		21	(0.37)	None	
Sodium Chloride...	175	(2.99)	153	(2.62)	175	(2.99)
	<hr/> 842 (12.26)		<hr/> 842 (12.26)		<hr/> 842 (12.26)	

It will be noted that each method gives different results on more than one constituent. In one method, certain salts are reported as present which are reported as absent in another method, yet all of these reports are based on the same analysis. It is evident that some of them must be misleading; as a matter of fact, all three of these reports are somewhat misleading, and the only report that shows exactly the composition of the water is the report given above in terms of ions. The common ions which occur in ground and surface waters admit of the following possible combinations: Calcium chloride; calcium nitrate; calcium carbonate; calcium bicarbonate; calcium sulphate; magnesium chloride; magnesium nitrate; magnesium carbonate; magnesium bicarbonate; magnesium sulphate; potassium chloride; potassium nitrate; potassium carbonate; potassium bicarbonate; potassium sulphate; sodium chloride; sodium nitrate; sodium carbonate; sodium bicarbonate; sodium sulphate.

CONVERSION OF UNITS

Sometimes it is desired to have the amounts of the salts in a water expressed in other units. An analysis is easily changed from one basis to another by use of a simple factor.

To convert parts per million to grains per U. S. gallon, multiply by .0583.

To convert grains per U. S. gallon to parts per million, multiply by 17.14.

To convert parts per million to pounds per 1000 gallons, multiply by .00833.

To convert grains per U. S. gallon to pounds per 1000 gallons, multiply by 7.

CONVERSION OF SALTS TO IONS

Since many analyses, particularly old analyses, are only available in terms of possible salt combinations, it is very often nec-

essary to calculate these reports back to the terms of the ions that were originally determined in the water. This can be done very easily by the use of gram-equivalents or percentage factors. The following method is simpler and more nearly in conformity with other simple engineering calculations. Multiply the salt by a factor which represents the percentage of the desired ion in the salt. This will give the amount of the desired ion. The difference between the amount of the ion and the original amount of the salt will give the amount of the other ion which went to make up the salt. Apply this procedure to each salt, collect like ions and add them, and the final result will be in terms of ions. Following is a practical example.

Given the following analysis in terms of salts, calculate to terms of ions.

Hypothetical Salt Combinations	Parts per Million
Calcium Sulphate	119
Calcium Carbonate	20
Calcium Bicarbonate	385
Magnesium Sulphate	143
Sodium Chloride	175

To calculate calcium sulphate, CaSO_4 , to calcium ion, Ca^{++} and sulphate ion, SO_4^{--} , multiply the amount of calcium sulphate by the factor, .2944. (29.44 per cent of calcium sulphate is calcium.)

$119 \times .2944 = 35$ parts per million calcium ion in calcium sulphate. Subtract the amount of calcium ion so obtained from the total amount of calcium sulphate and the result will be the sulphate ion in this salt.

$119 - 35 = 84$ parts per million sulphate ion in CaSO_4 .

Calculate calcium carbonate to calcium ion and carbonate ion.

$20 \times .4004 = 8$ parts per million calcium ion in CaCO_3

$20 - 8 = 12$ parts per million carbonate ion in CaCO_3

Calculate calcium bicarbonate to calcium ion and bicarbonate ion.

$385 \times .2472 = 95$ parts per million calcium ion in $\text{Ca}(\text{HCO}_3)_2$

$385 - 95 = 290$ bicarbonate ion in $\text{Ca}(\text{HCO}_3)_2$

Calculate magnesium sulphate to magnesium ion and sulphate ion.

$143 \times .2020 = 29$ parts per million magnesium ion in MgSO_4

$143 - 29 = 114$ parts per million sulphate ion in MgSO_4

Calculate sodium chloride to sodium ion and chloride ion.

$175 \times .3935 = 69$ parts per million sodium in NaCl .

$175 - 69 = 106$ chloride ion in NaCl .

Collecting the ions:

Calcium	$(35 + 8 + 95) = 138$
Magnesium	$= 29$
Sodium	$= 69$
Carbonate	$= 12$
Bicarbonate	$= 290$
Sulphate	$(84 + 114) = 198$
Chloride	$= 106$

These results check with the original data from which the analysis was calculated. This method may be applied to the recalculation of any analysis reported as hypothetical salt combinations.

TABLE OF FACTORS FOR CALCULATING IONS FROM SALTS

The factor in each case corresponds to the percentage of the ion in the salt. For instance, potassium chloride, KCl , consists of 52.44 per cent of potassium ion and 100 per cent—52.44 per cent or 47.56 per cent of chloride ion.

KCl to K5244	MgCl to Cl7446
KCl to Cl4756	$\text{Mg}(\text{NO}_3)_2$ to Mg1640
KNO_3 to K3866	$\text{Mg}(\text{NO}_3)_2$ to NO_38360
KNO_3 to NO_36134	MgCO_3 to Mg2884
K_2CO_3 to K5658	MgCO_3 to CO_37116
K_2CO_3 to CO_34342	$\text{Mg}(\text{HCO}_3)_2$ to Mg1662
KHCO_3 to K3905	$\text{Mg}(\text{HCO}_3)_2$ to HCO_38338
KHCO_3 to HCO_36095	MgSO_4 to Mg2020
K_2SO_4 to K4487	MgSO_4 to SO_47980
K_2SO_4 to SO_45513	CaCl_2 to Ca3610
NaCl to Na3935	CaCl_2 to Cl6390
NaCl to Cl6065	$\text{Ca}(\text{NO}_3)_2$ to Ca2442
NaNO_3 to Na2706	$\text{Ca}(\text{NO}_3)_2$ to NO_37558
NaNO_3 to NO_37294	CaCO_3 to Ca4004
Na_2CO_3 to Na4340	CaCO_3 to CO_35996
Na_2CO_3 to CO_35660	$\text{Ca}(\text{HCO}_3)_2$ to Ca2472
NaHCO_3 to Na2738	$\text{Ca}(\text{HCO}_3)_2$ to HCO_37528
NaHCO_3 to HCO_37262	CaSO_4 to Ca2944
Na_2SO_4 to Na3238	CaSO_4 to SO_47056
Na_2SO_4 to SO_46762	Fe_2O_3 to Fe6995
MgCl_2 to Mg2554	Al_2O_3 to Al5303

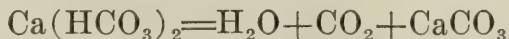
3. Scaling

WHAT MAKES SCALE

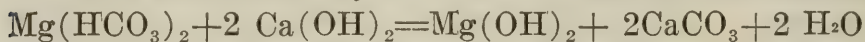
The chief producers of boiler scale in filtered water are the salts of calcium and of magnesium. Of course, mud or suspended matter that is allowed to get into a water supply will form scale, and silica in dissolved or colloidal form (that is, not in actual solution, but so finely divided that its suspension behaves like a solution and cannot be removed by filtering) will also go to make up scale. Generally the amount of silica in a water is very small, although one instance has been cited in which a water carried nearly five hundred parts per million (30 grains per U. S. gallon) of silica, and gave a scale that was like glazed porcelain. Iron and aluminium, though both scale formers, are not important, because they are present only in small amounts in most waters.

CLASSES OF HARDNESS

Thus it appears that the big scale forming constituents are the lime and the magnesia compounds. These constitute two classes of "*hardness*." The first class is composed of the bicarbonates of calcium and magnesium, and is called "*temporary hardness*." In other words, if the water contained only calcium and magnesium ions and bicarbonate ions, this water would have only temporary hardness. As has been pointed out above, if a water containing these ions is *boiled*, the bicarbonate ions will decompose into water and carbonate ions according to this equation:



The insoluble calcium carbonate will be formed and will precipitate, i. e. will appear in solid form. Since magnesium carbonate is appreciably soluble, it is usually not precipitated through this action. But in the chemical treatment to remove temporary hardness, the bicarbonates are decomposed by the addition of lime, and this reacts with magnesium bicarbonate to form the insoluble magnesium hydroxide according to this equation.



Hence magnesium bicarbonate is considered to be a part of the temporary hardness.

The second class of hardness is known as "permanent hardness." It is due to an excess of calcium and magnesium ions over the amount that will combine with the bicarbonate ions. The negative ions for this excess of calcium and magnesium ions may be sulphate, chloride or nitrate ions. Ordinary boiling does not affect this class of hardness. Only under boiler conditions—that is, high temperatures resulting from heavy pressures—do these salts separate as a scale, either in their original condition (as is the case with gypsum) or decomposed to a hydrate or oxide (as is the case of magnesium salts). For details concerning these actions see the description of the properties of salts given above. It is often stated that temporary hardness alone will form a sludge or a soft scale, permanent hardness alone produces a very hard scale, and that the quality of the scale depends on the relative amounts of the two kinds of hardness. As a matter of fact, the thing is not nearly so simple as that. Under some conditions temporary hardness no doubt forms a sludge, but there are cases where it forms scale which is quite dense and very hard. On the other hand, a few instances have been given where permanent hardness (gypsum for instance) has given a soft scale. It is very difficult to tell where loose and non-adhering scale leaves off and true scale begins. Generally, hard waters contain both kinds of hardness, and hence form scale. The type of boiler, the pressure, the rate of operation, the degree of concentration allowed before "blowing off" (i. e. emptying the boiler), the load maintained, all are just as much factors in the nature and amount of scale as the constituents of the water.

EFFECT OF OIL

Another phase of the scaling problem not often mentioned is the effect of a thin film of oil. It has been estimated that the insulating power of a thin film of oil is much more than that of a scale averaging one-sixteenth of an inch in thickness. Besides this, the scale that is formed by the collecting of light floating material by the surface film of the oil and its settling on the heating surface is even worse than ordinary scale, because it causes corrosion as well as loss of heat. This corrosive effect

is of such importance that it will be taken up later under a special heading.

FORMULAS FOR SCALE

Formulas have been prepared by Dole and Stabler of the U. S. Geological Survey, which take care of the amount and quality of scale from a given water. These formulas give a reasonably accurate estimate of the amount of scale, and some idea as to whether or not it will be a hard scale. Suspended matter, which means the mud, clay and vegetable matter that can be removed by filtration, is summed up under the symbol "Sm." Naturally, if a filter is used, the suspended matter must be left out of the calculation of the amount of boiler scale. Silica, and any colloidal material, such as suspensions of clay in a state of extremely fine subdivision, which a filter will not remove without the use of a coagulant (the danger from the use of coagulants in excess is discussed under Corrosion) is called colloidal matter "Cm." The other symbols have already been explained. The amounts of each constituent to be used in these formulas must be expressed in *parts per million*. Most analyses by ions are reported in this value. If they are in grains per U. S. gallon, multiply by the factor 17.14 and obtain parts per million. The formula which gives the total amount of scale (Sc) is as follows:

$$\text{Sc} = .00833 \text{ Sm} + .00833 \text{ Cm} + .0107 \text{ Fe} + .0157 \text{ Al} + .0138 \text{ Mg} + .0246 \text{ Ca}.$$

In most cases the formula may be reduced to the following form, which leaves out iron, aluminium and suspended matter, and includes only colloidal matter (which is considered to be all silica.)

$$\text{Sc} = .00833 \text{ SiO}_2 + .0138 \text{ Mg} + .0246 \text{ Ca}$$

The result in either formula is expressed in pounds per thousand gallons, which is the term most commonly used in boiler calculations.

In order to find out how much hard scale (Hs) will be formed, the following formula has been suggested:

$$\text{Hs} = .00833 \text{ SiO}_2 + .0138 \text{ Mg} + (.016 \text{ Cl} + .0118 \text{ SO}_4 - .0246 \text{ Na})$$

The amount of hard scale divided by the total amount of scale gives the percentage of hard scale, or what is called the *coeffi-*

cient of scale hardness. This may be regarded as a valuable approximation under some conditions, but is not to be considered as a hard and fast rule to be applied and relied upon in any and all cases. The scale is classed as soft if the percentage is below 25 per cent, if between 25 per cent and 50 per cent it is called medium, and anything over 50 per cent is called hard scale. As has been pointed out, the nature of the scale cannot always be determined from formulas. Some waters that would give a soft scale under one set of boiler conditions may give a wholly different sort of scale under other conditions. However, it may be said that the amount of scale produced need not be determined with any degree of accuracy. It is only necessary to know the approximate amount of scale and something of its nature. The main thing in which an engineer is interested is the removal of scale and the effect of scale. This matter will be taken up in the following chapter.

CALCULATION OF SCALE FROM FORMULAS

The application of the formula for scale to a typical water analysis will illustrate the general method of such calculations. Take as an example the water analysis given above. Add 26 parts per million of silica (SiO_2), which was obviously to be left out in a discussion of the formation of salts.

	Parts per Million
Calcium	138
Magnesium	29
Sodium	69
Carbonates	12
Bicarbonates	290
Sulphates	198
Chlorides	106
Silica	26

The abbreviated Stabler-Dole formula for scale would give this result:

$$\begin{array}{rcl}
 26 \text{ (Silica)} \times .00833 & = & .22 \\
 29 \text{ (Magnesium)} \times .0138 & = & .40 \\
 138 \text{ (Calcium)} \times .0246 & = & 3.39
 \end{array}$$

4.01 pounds of scale per 1000 gallons

The formula for hard scale gives these results:

23	(Silica) \times .00833	= .22
29	(Magnesium) \times .0138	= .40
106	(Chlorides) \times .0160	= 1.70
198	(Sulphates) \times .0118	= 2.34
		<hr/>
		4.66
69	(Sodium) \times .0246	= 1.70
		<hr/>

2.96 pounds of hard scale per 1000 gallons

4.01 divided into 2.96 gives 73.8%, which is the coefficient of scale hardness for this water. As noted before, this formula for hard scale does not take into account many other factors, such as type of boiler, rate of evaporation, pressure, etc., and as a result is only of an indicative or approximate value.

If the methods of hypothetical combination are employed, varying results are obtained, ranging from 3.76 to 4.32 pounds of scale per thousand gallons. The main point of difference between various chemists in their methods of calculation seems to be in the form in which magnesium is considered to be present in the scale. If reported as an oxide, a lower figure will be gotten than if reported as a carbonate. The Stabler-Dole formula gives a result which is the mean of these, and represents fairly closely the amount of scale formed from a given water, the analysis of which is reported in ionic form.

EFFECTS OF SCALE

(a) *Space Loss*.—The next thing to consider is the various effects of scale. One of the first effects to be pointed out is the decrease in heating surface which scale produces. Of this Dr. Greth has given a striking example. A certain 300 H. P. boiler contained 3000 square feet of heating surface. It had 146 four-inch tubes, 18 feet long. The internal tube circumference was 11.75 inches. Suppose scale to form $\frac{1}{4}$ inch thick. The internal tube circumference is cut down to 10.18 inches, and there is a loss of 18.8 square inches of heating surface for every foot of tube length, or a total loss of 343 square feet of heating surface. On the basis of the whole boiler this amounts to a loss of 11.4%. Even an eighth of an inch of scale gives a loss of 5.7%, and when the scale gets up to $\frac{3}{8}$ inch in this boiler, the loss is 17.4%. This simply means that the boiler has shrunk in size to this amount.

(b) *Heat Loss.*—The most important effect of scale is due to the fact that it is a wonderful heat insulator. Its chemical composition seems to have little to do with its heat insulating power, the big question being the density or mechanical structure of the scale. A series of experiments by Professor Schmidt of the University of Illinois gave the following results:

Character of Scale	Thickness	Composition	Loss of Efficiency
Hard	1/50"	Mostly Carbonate	9.4
Soft	1/32"	Mostly Carbonate	7.2
Hard	1/32"	Mostly Carbonate	8.5
Soft	1/25"	Mostly Carbonate	8.0
Hard	1/25"	Mostly Sulphate	9.3
Hard	1/20"	Mostly Sulphate	11.1
Soft	1/16"	Mostly Sulphate	10.8
Soft	1/16"	Mostly Carbonate	11.0
Soft	1/16"	Mostly Carbonate	12.4
Hard	1/16"	Mostly Carbonate	12.6
Soft	1/11"	Mostly Carbonate	15.0
Hard	1/9"	Mostly Sulphate	15.9

Regarding the heat insulating effect of scale, this statement is made by E. W. Fiske:

"If the rate of evaporation is low, and especially if the scale in question is in a part of the boiler or its auxiliaries where the flue gases have lost some of their heat, and the feed water has not reached its maximum temperature, the scale will be damp to some extent. If, however, the rate of evaporation is high, the body of the scale will be dry, or contain nothing but highly heated superheated steam, and in this condition it approaches the condition of a dry pipe covering, and we have an excellent insulator, which, considering its thickness, compares favorably with pipe coverings in general. This may account for the fact that tests made at high rates of evaporation generally show decided loss on account of scale."

(c) *Cost.*—This loss of fuel efficiency can be counted directly in dollars and cents. Think of losing 16% out of every ton of coal, used in forcing the heat through insulating scale. This means *sixteen cents on every dollar*, and all on account of a scale of the apparently trifling thickness of *one-ninth of an inch*. Consider further the cost and trouble and worry and damage in getting scale out of boilers. The life of flues or tubes is

shortened by letting them get scaled and then cleaning them. Repair costs increase. There is constant danger of accumulation of scale at one spot, overheating of the boiler steel at that point to a temperature where it will soften and give way. If it goes no further than this "bagging," it is bad enough. This very thing is the cause of numerous fatal boiler explosions.

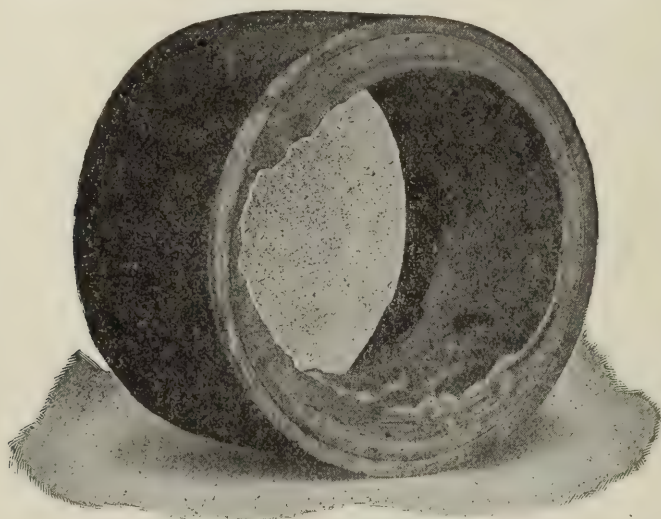


Fig. 2. Section of tube from a badly scaled boiler.

An idea as to the cost of maintaining scaling boilers may be gotten from data which was given in an article in *Power*, May 23, 1916, in which a record is given of the cost of cleaning a B. & W. boiler, operating at 200 pounds pressure. The work was done by means of a water turbine.

Size of tube in inches.....	4
Number of tubes	287
Boring time in hours.....	13.5
Approximate thickness of scale in inches.....	3/32
Cost of cutter wheels.....	\$3.00
Cost of water, 9000 cu. ft. at 18c. per 1000 ft..	\$1.62
Cost of labor.....	\$8.72
Cost of steam to pump water, 4942 pounds at 12.5 cents per 1000 pounds.....	.62
Cost of oil.....	.60
Cost of cleaning tubes per boiler.....	\$14.56

The weight of the steam was figured on the displacement of the pump, with a 10% allowance for condensation losses. These

estimates are said by other engineers to be too low on the basis of average conditions, since this was a special speed test, and included only the turbinizing of the tubes and taking off and replacing of caps. It did not include the washing out of the drum. In commercial work, the cost would be about twice as much as quoted in the table.

Another author has summarized the cost due to scale as follows:

"The extra coal consumed; the cost of extra boilers to make up for the limitations on boiler capacity imposed by scale-forming water; the cost of extra boilers in order to provide stand-by for cleaning; the cost of cleaning, retubing and repairing boilers; the cost of firing boilers put out of service for repairing and cleaning; the depreciation on boilers, the life of which is greatly shortened by

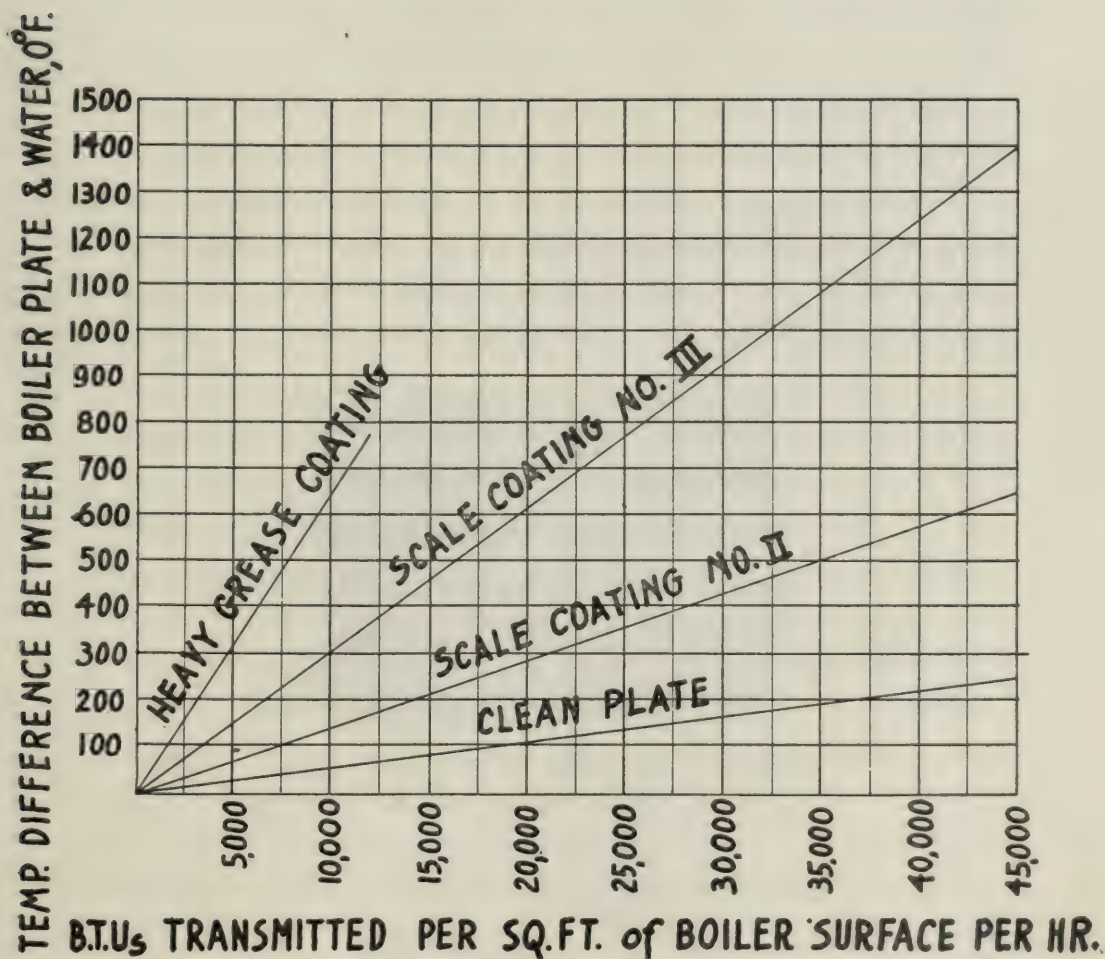


Fig. 3. Effect of scale on heat transmission.

corrosion, pitting, cleaning, expansion and contraction strains, and other evil effects of scale-forming feed water."

There is no excuse for scale with all that is known today about boiler treatment and outside softening. Many plants install expensive machinery and all manner of labor-saving devices, and time clocks, and efficiency methods, all of which are modern and commendable, but waste from 10% to 20% of their fuel in firing scaled boilers. The progressive steam user is going to begin his efficiency and economy right at the original source of waste.

It has thus been shown what causes scale, how the amount and nature of scale can be figured from an analysis, and what the effects of scale are. But before taking up the question as to how to remedy the difficulty, other diseases of the boiler due to bad water must be presented.

4. *Corrosion*

The phenomena of corrosion are very familiar to all steam engineers. Considerable patches of the boiler metal may be eaten away to a very slight depth; there may be very marked effects around bolt heads and seams; or there may be small cir-

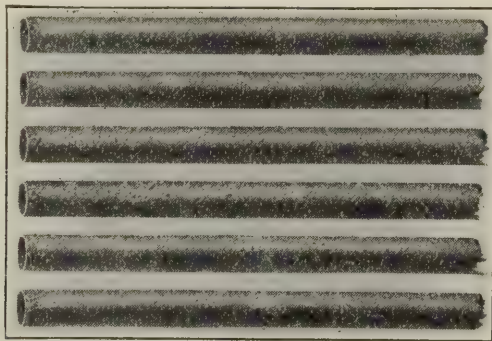


Fig. 4. Example of external corrosion and pitting.

cular pits of considerable depth, these last named being frequently found under scale. Most corroded and pitted boiler surfaces are found below the water line.

CAUSES OF CORROSION

(a) *Free Acid*.—Any water that contains free acid will cause corrosion. Sulphur waters in Texas are rarely acid, since they usually come from or through a limestone formation, where the free sulphuric acid is neutralized and converted into calcium sulphate or gypsum. As stated before, out of a very large number of waters analyzed in Texas, only a very few were found to contain free acid. Such waters, however, are very common in coal bearing regions.

(b) *Magnesium Salts*.—Magnesium salts cause corrosion. The chloride of magnesium has always been recognized as a corrosive salt, since under boiler conditions it reacts readily with water to form magnesium hydroxide and hydrochloric acid. The former is very insoluble and goes into the scale, while the latter corrodes the iron. Magnesium sulphate behaves in the same way. Only that part of the magnesium ion that is in excess of the amount corresponding to the carbonate and bicarbonate ion causes corrosion. Hence the addition of carbonate ions (added as sodium carbonate in the lime-soda process) stops this effect.

(c) *Gypsum Scale*.—While there is considerable uncertainty on the question, it seems very likely that a calcium sulphate, or gypsum, scale causes corrosion, because the heat insulating effect of scale is such that the part of the scale next to the boiler iron attains a high temperature, the calcium sulphate decomposes to give calcium oxide, sulphur dioxide and oxygen, and the oxygen attacks the metal. It has been observed that this effect is only marked when the scale is thick.

(d) *Oil*.—The effect of "oil scale" is somewhat similar. When oil is allowed to get into the boiler, it picks up the light and floating impurities on the surface, and the mixture settles out and sticks to the iron of the boiler. There it bakes and burns and produces dangerous and excessive corrosion.

(e) *Gases*.—Some dissolved gases play an important part in steam boiler corrosion, the two chief offenders being carbon dioxide and oxygen. At one time, carbon dioxide was considered one of the big causes of trouble. Under modern boiler practice, where *open* feed water heaters are largely used, very little of this gas gets into the boiler. The carbon dioxide, com-

ing from the decomposition of the various bicarbonates, is given off slowly, and is diluted with too much steam to do much damage. In *closed* feed water heaters, and particularly in closed hot water "house-heating" systems, there is serious trouble from this source. Frequently there is so much of this gas present that it settles on the surface of the iron in bubbles. The solution of the gas is, of course, most concentrated where the bubbles appear, and hence causes most corrosion at this point. Wherever there was a bubble, a "pit" is formed. The effect of dissolved oxygen will be noted in another connection.

(f) *Galvanic or Electrolytic Action*.—A big cause of corrosion is the galvanic action (or electrolytic action) which takes place in boilers. To understand this, let us consider the construction of an ordinary battery cell, which is familiar to engineers. Any two different metals in a salt solution, when connected, will set up galvanic action, even though it may be too feeble to be ordinarily noticeable. Suppose a piece of mill scale, slag, sulphur or manganese is at the surface of the boiler iron, and in contact with the salt solution, which ordinary ground or surface waters are. The piece of mill scale, slag, etc., will act as one pole; a spot of pure iron on the surface of the boiler wall will act as the other pole; they are both "dipped" into the liquid extending from one to the other (which serves as the battery liquid); and the iron plate to which they are attached serves as the "connecting wire" through which the electric current flows. One of the above two spots—the positive pole—will act just like a zinc pole in a battery cell, and the material there will be consumed or corroded away gradually. At the other spot—the negative pole—hydrogen will be evolved, or will be oxidized to water by free oxygen present in the water. Any difference in the crystalline structure or chemical composition of the steel in different parts of the boiler or difference in structure due to mechanical strains or deformations (such as occur in punching rivet holes) give these different spots the property of acting as opposite poles of a galvanic cell.

(g) *Oxygen*.—When corrosion takes place, a certain amount of hydrogen gas is formed at the negative pole. When free acid attacks iron, the metal goes into solution and the hydrogen of

the acid appears as a gas. This may cover the surface of the metal as a protecting film and slow down and stop the action, an effect well illustrated in the polarizing of battery cells. But

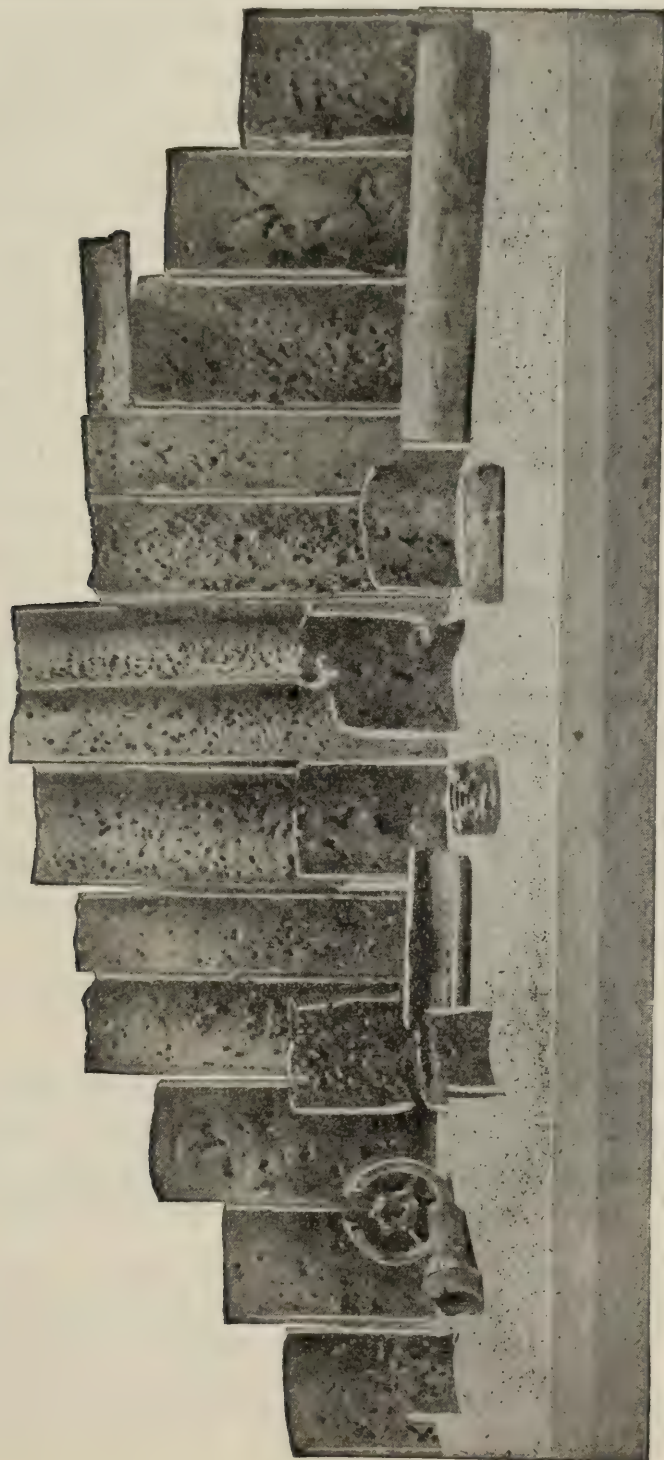


Fig. 5. Example of internal corrosion and pitting.

if there is dissolved oxygen in the water, or substances which give up oxygen easily—i. e., nitrates—in the water, then this film of hydrogen is continually removed by simple oxidation, and the corrosive action progresses more rapidly. Hence oxygen may be spoken of as a “stimulating factor” in corrosion.

(h) *Alum Coagulants*.—In this connection, it is well to call attention to the danger that may result and has resulted in many cases from the use of coagulants, especially when used in excess in order to clear muddy water. The principal coagulating agent is sulphate of aluminium or ordinary alum. Unless there is sufficient alkali present to neutralize it, the sulphuric acid produced by the reaction of alum with hot water will attack and ruin the boiler. Only small amounts of coagulants are necessary with an efficient filter, and if the water is closely watched and always kept slightly alkaline, this danger is prevented.

FORMULA FOR CORROSION

As has been stated, it is impossible to foretell from the analysis of a water alone whether or not corrosion will take place when the effect is due to galvanic or electrolytic action. However, it is possible to tell with a very reasonable degree of probability *whether the ions present are of the kind that produce acid effects in a boiler*. To calculate the corrosion possible from this source, the best corrosion formula at present available is that of Stabler, given below:

Coefficient of Corrosion (C) = $H + .1116 \text{ Al} + .0361 \text{ Fe} + .0828 \text{ Mg} - .0336 \text{ CO}_3 - .0165 \text{ HCO}_3$

By this, the probability and degree of corrosion, due to acid forming constituents, may be calculated from the ions present. Of course no account whatever can be taken in such a formula of corrosion due to galvanic action or to the effects of dissolved gases.

According to the formula of Stabler, the following is the classification of waters according to their acid forming tendencies.

1. **Corrosive.** If the coefficient be positive the water will certainly corrode the boiler.

2. **Non-corrosive.** If the coefficient plus the factor .0503 multiplied by the amount of calcium ion present (expressed in parts per million) is negative, no corrosion will take place due to acidity.

3. **Semi-corrosive.** If the coefficient is negative, but the coefficient plus .0503 times the calcium is positive, corrosion due to acidity may or may not occur, the probability of corrosion varying directly with the value of the expression: coefficient of corrosion plus .0503 times the calcium.

Given a typical analysis:	Parts per Million
Calcium	85
Magnesium	69
Sodium	50
Iron	6
Aluminium	4
Carbonates	6
Bicarbonates	359
Chlorides	170
Sulphates	57

Employ the formula of Stabler.

4 (Aluminum)	$\times .1116 =$.45
6 (Iron)	$\times .0361 =$.22
69 (Magnesium)	$\times .0828 =$	5.71
		<hr/>
		6.38
6 (Carbonates)	$\times .0336 =$.20
359 (Bicarbonates)	$\times .0165 =$	5.92
		<hr/>
		6.12
		<hr/>
		6.38
		6.12
		<hr/>
		+.26

Since the coefficient of this water is positive, even though small, it will cause some corrosion.

In order to show the disadvantage, in this connection, of an analysis reported with ions combined arbitrarily to certain salts, calculate the "hypothetical combinations" by one of the general methods. The following results will be obtained for the above analysis.

	Parts per Million
Sodium Chloride	127
Magnesium Chloride	125
Magnesium Sulphate	72
Magnesium Bicarbonate	138
Calcium Bicarbonate	324

From this statement of the composition of the water, it appears to be decidedly corrosive, due to the presence of magnesium salts other than carbonates, while in reality it is only slightly corrosive.

While the Stabler formula fails in that it does not take account of any other cause of corrosion but acidity, it is very valuable as far as it goes. Any water that gives a corrosive or semi-corrosive coefficient by this formula should be treated chemically outside the boiler so as to remove the cause of corrosion, and in the boiler *a slight alkalinity of the water should be rigidly maintained.*

EMBRITTLMENT OF STEEL BY CAUSTIC SODA

Within the last two or three years, a number of boiler explosions have been charged to the embrittlement of steel from caustic soda, as the result of using artesian waters containing carbonate of soda, or boiler compounds in excess which are made up largely of this salt. While we are not at liberty to publish the details of the experiments made by an Eastern manufacturing concern of international reputation, we have gone over their results and give below some conclusions drawn from these results, the publication of which is authorized by the firm making these experiments.

The effect of caustic soda seems to manifest itself in small, hair-line cracks in the seams below the water line, always starting from a joint, and in many cases so small that they could not be discovered without removing the rivets. The metal of the boilers so affected seems to lose, in the parts that are so damaged, its toughness, and becomes quite brittle. One plant switched from a creek water containing no sodium carbonate to an artesian water carrying a little short of 12 grains per gallon, and immediately began to have trouble with embrittlement. More than twenty cases were reported in one region, and all the troubles had the common characteristic of being in distinct geographical districts, all were below the water

line, and all in boilers using artesian water. In these districts where gypsum occurred in the water, there was no trouble with cracking reported, and it is to be noted for chemical reasons that where gypsum occurs, sodium carbonate will be absent. It seems evident that the material of the boiler was not at fault, since the same trouble happened with plates from various sources and of different form. The boilers affected represented several different leading and reputable makers, and it is hardly likely that all of them could have put out unreliable products in the same region or at all. The designs were as different as the makes. All manner of operating conditions obtained, without altering the cracking and embrittling troubles. The characteristics are all the same, the cracks being alike, and differing from cracks from all other causes, that have from time to time been found in steam boilers. All were below the water line and in seams. All the boilers, with one exception, were fed with artesian water, the one ingredient common to all being sodium carbonate, which changes in part at least to the hydrate or caustic soda, and, depositing in the seams, sets up corrosion. The hydrogen that is freed is absorbed or occluded by the steel, and brittleness is produced. Water taken from a boiler in service which showed this trouble had nearly 250 grains of sodium carbonate per gallon. Serious trouble occurred in a boiler using a compound made up largely of soda ash and caustic soda. In this case the water was almost pure except for the presence of the solids due to the compound, and in general it may be stated that there is no evidence to show that by the use of soda compound for treating waters where there are substances in the water with which reaction can take place, and where the treatment is not to excess, any trouble of this kind has occurred. In the case just cited, the cracks were so small that they could not be seen until the iron was cleaned. Magnesium sulphate was used in a number of cases in order to get rid of the excess of sodium carbonate. The cracking and embrittlement seem to have ceased as the result of such treatment. The whole trouble appears to be due to occluded hydrogen.

A great deal of work is being done just now on this subject, the results of which will be watched with much interest by boiler water users. In the meantime, if the alkalinity of the boiler water is continually kept down to a few grains per gallon, it seems quite certain that there is no danger to users of lime soda softeners.

CORROSIVE EFFECT OF VERY PURE WATER

Absolutely pure water is rather corrosive for another reason. Its solvent power is unusually great, hence it dissolves iron appreciably. However, the addition of a little alkaline material prevents the dissolution of iron.

HOW TO PREVENT CORROSION.

All this may sound rather dangerous and terrifying to the steam user, but, as a matter of fact, corrosion can be very easily guarded against and prevented. The free acid can be neutralized by just the right amount of alkali; the magnesium, iron, and aluminium salts can be gotten rid of by proper softening and treatment; dissolved gases usually escape for the most part from the open feed-water heater; the water can be maintained in a slightly alkaline condition; boilers can be made of a high grade iron, so free from impurities that it will not set up galvanic action; and correct boiler design can prevent causes due to faulty construction. A properly softened water freed from gases in the right kind of a preheater and fed into a boiler of the right material and construction, will not cause corrosion.

The common-sense thing to do is not only to test the feed water to see if it carries corrosive constituents, and then use preventatives, but above all things *to test water in the boiler*, to ascertain whether or not it is developing conditions that will make corrosion possible. Slight alkalinity of the boiler water should be maintained, tendencies to acidity being continually corrected by use of soda ash.

5. *Foaming*

The common boiler trouble known to engineers as "foaming" is a familiar one. Since there seems to be some confusion between the terms "foaming" and "priming," the liberty is taken here of quoting from a letter from R. C. Bardwell, Chief Chemist of the Missouri Pacific.

FOAMING AND PRIMING DEFINED

" '*Foaming*' consists of the steam bubbles building upon the surface of the water, instead of breaking and freeing steam. It becomes serious when the bubbles build up so rapidly and hang together long enough to reach the point where dry steam is supposed to be taken off, starting a sort of siphoning action, and considerable water is carried over with the steam."

" '*Priming*' is the sudden evolution of steam from the heating surface, similar to 'bumping' in laboratory apparatus, and

is due either to poor design of the boiler, and its being worked beyond its capacity, or to the sudden opening of the throttle. This is altogether different from foaming, and can be mechanically controlled to a large extent."

CAUSES OF FOAMING

It seems practically certain, however, that the main cause of foaming is *not due* to the concentration of soluble material in the water. Clean, clear water, free from all suspended matter, vegetable matter, and oil will not cause foaming under any reasonable conditions of concentration. The idea that foaming is due to an increase of surface tension because of increased concentration of soluble salts is not borne out by theory or facts. The surface tension of the solution of any salt normally in boiler feed water at the concentration allowable in ordinary boiler practice (never over 3% to 4%) is so near that of pure water that the variation is negligible.

(a) *Suspended Matter*.—It is not at all a question of surface tension, but rather of *viscosity* of surface films. A soap solution has only a fraction of the surface tension of pure water, but it is sure to cause foaming. It is known from extensive experience on the part of many engineers that finely divided suspended matter will undoubtedly cause foaming. This is not due, as often wrongly stated, to the action of each small particle as a "steam point." The colloidal solid matter gives mechanical strength or tenacity to the liquid in the thin films formed over bubbles, and hence the steam bubbles rising to the surface retain their films and collect to produce foam.

(b) *Alkalies*.—Sodium carbonate is considered as the chief offender among salts thought to cause foaming. The most probable explanation of its action is, first, that it loosens old scale, and thus adds to the suspended matter; and second, that because of its alkalinity, it produces from the suspended matter a slightly gelatinous, glue-like, viscous solution, manifesting its effect in the surface-film, from which bubbles of steam will form foam.

This opinion, then, considers that both the suspended matter and the means for putting it into viscous or emulsified form (which is done by salts like sodium carbonate) enter into the

causing of steam boilers to foam. Very few boilers are ever free from suspended matter or dirt of some sort, and as the concentration of the soluble salts increases, the effect of the loose sludge becomes more marked.

(c) *Boiler Defects.*—There are still other causes of foaming besides those already given. Boiler construction and boiler operation have a great deal to do with foaming. One boiler will give perfect service even up to abnormally high concentration of solids; and another boiler with the same feed water will foam in a day's service. Some boilers are so badly made that they will "prime" with the slightest excuse. Some boilers are so well built that they will stand up and give service with almost any kind of a water. Pressure has much to do with foaming. As a rule, the heavier the pressure carried, the greater will be the likelihood of foaming. The rate of operation and sudden variations in load are to be considered in accounting for foaming. The problem is by no means simple, and each boiler and each water supply must be worked out individually.

HOW TO PREVENT FOAMING

The main thing which interests steam users is not the cause of foaming, but its prevention. In the first place, muddy water should be kept out of the boiler.

(a) *Filtering and Softening.*—Filters are cheap in first cost, and practically cost nothing to operate. A water that will form sludge or scale in any amount has no business in a boiler.

(b) *Blowing Down.*—Concentrations of dissolved salts can be held below reasonable limits by partially emptying the boiler frequently (or to use the engineer's term, "blowing down"). The rate and amount of emptying should be regulated not only by the type of boiler and rate of evaporation, but by the amount of dissolved material in the feed water. It is obvious, all other conditions being equal, that a water carrying a thousand parts per million dissolved solids should call for blowing down twice as often as one with five hundred parts per million. Following a practice of lowering the water level by blowing down a certain distance at arbitrary time intervals (for instance, so many gauges every so many hours) regardless of the nature of the

water supply is utter foolishness on the part of any engineer. It is true that blowing down means loss of heat and consequent loss in fuel, and it should only be done when it is necessary. But this loss is not to be compared to the value of the protection of engines and turbines from water coming over. Better a few dollars more on the coal bill than a wrecked engine or a stripped turbine. An engineer who uses his head will soon learn how much his boilers will stand with a certain water supply, and will stay within limits.

(c) *Skimmers and Traps*.—Since most of the suspended matter that causes trouble is on the surface of the water, mechanical devices, such as skimmers and surface blow-off, are often successfully resorted to. As a final protection, adequate water traps in the steam line will save the engine or turbine, if foaming is sudden or unexpected, until the cause can be gotten at and removed. This is an engineer's problem, and not a matter for a chemist to decide, or even to discuss.

(d) *Anti-Foaming Compounds*.—Unless a boiler is to be washed out reasonably often it is best to rely on such mechanical means just referred to, rather than anti-foaming compounds. Most of such compounds are not only utterly without value, but are dangerous and destructive to boilers. There are some few legitimate compounds, made up mainly of castor oil and tannin, that have some virtue, but they are to be used only sparingly and then only with a chemist's advice and supervision. The practice of putting mineral oil, paraffin, ozokerite, and like substances in a boiler is as dangerous as it is foolish. These things may stop foaming a little while but the man who uses them pays a big price in the way of corrosive oil scale and "bagged" flues or tubes.

FOAMING FORMULAS

Formulas for determining whether or not a certain water will foam have been devised, but these leave out so many factors that their author admits that they have a very doubtful and extremely limited value. Hence they are not given here.

In general it may be said that a clean water, free from scale and sludge-foaming constituents can be successfully handled in a decently constructed and sensibly operated boiler, unless it

contains much alkali. In that case the heavier the constituents are, the more the boiler has to be blown down. Only a few waters in Texas, these mainly artesian, cannot be handled by a common-sense engineer, once he knows that he must have a clean, soft water.

CHAPTER TWO

HOW TO STOP BOILER TROUBLES DUE TO BAD WATER

The various causes of boiler trouble have been discussed in considerable detail. The question that will immediately follow is how to stop boiler troubles or reduce them to their smallest possible extent. Like diseases, each trouble has a specific remedy, and it is impossible to lay down general methods and directions that will absolutely fit all cases. Each individual problem is a study in itself. It is possible, however, to outline the general remedies employed in getting rid of costly and troublesome boiler ailments.

1. Boiler Compounds

In spite of modern advancement, the notion is still extremely prevalent that if the right kind of chemical or combination of chemicals can be found and put into a steam boiler, all troubles will be at an end. All manner of substances have been used in steam boilers under the general head of Boiler Compounds. Some few of these have had a limited efficiency but in the main they have been ridiculous and dangerous remedies. In most cases, boilers have been ignorantly and indiscriminately "dosed," a practice that cannot be too severely condemned. In general the theory of boiler compounds is wrong. The water should as a rule be treated outside of the boiler. If a compound is used, it should be under the advice of a competent chemist, who has picked it out as the best available method of correcting the trouble, and then only in stated and correct amounts.

COMMON CHEMICAL INGREDIENTS

In the compounds used to prevent scaling, the most common ingredient is carbonate of soda or "soda ash." By introducing carbonate ion, the calcium and magnesium ions which cause

sealing are largely removed from solution as insoluble salts in the form of a loose sludge. Sodium phosphate has the same general action, but being more expensive than soda ash, it is rarely used. Barium salts, which may be used to remove sulphates, are also quite costly, and are hence rarely found in boiler compounds. These comprise about all of the efficient substances that are used in boilers to convert sealing constituents to a loose and non-adhering sludge.

SOME TYPICAL BOILER COMPOUNDS

Mr. Dudley K. French has very kindly furnished the author with copies of numerous analyses of boiler compounds concerning which he says: "Some of the greatest fakes are sold on the basis of the story of some wonderful discovery not understood by science at large, but fallen upon by sheer luck. Most of them depend upon the credulity of the engineers for their success."

For the benefit of those who have often in the past trusted blindly to boiler compounds without knowing what they contained or their chemical effects, a number of these analyses are given together with comments on their value or utter lack of value as remedies for boiler trouble. All of these compounds have been on the open market during the past ten or fifteen years, and the analyses are made from actual samples taken from the marketed products. No names or brands are quoted.

1. Dark colored liquid, neutral reaction.

Water	98.35
Vegetable Matter	1.28
Ash37

The vegetable matter is too small in amount, even if it were tannin, to be of any value. No comment is necessary on the water.

2. Thin, orange-yellow, very limpid liquid.

Water	90.73
Bichromate of Potash.....	8.89
Undetermined Matter38

The bichromate of potash is intended to prevent corrosion, but is very expensive. No comment is necessary on the water. To allow a corrosive water to go into a boiler, some chemist has said, is like deliberately poisoning a man and then giving him an antidote.

3. Very thin, reddish-brown solution with slight alkaline reaction.

Water	90.37
Carbonate of Soda.....	7.05
Chloride of Soda.....	.47
Organic Matter	1.49
Undetermined Matter62

The organic matter seems to be present largely to give a mysterious color to the compound, as it contained only traces of tannin. Why buy a dirty and very dilute solution of soda ash, when the pure salt is on the market?

4. Light-yellow, very limpid liquid.

Carbonate of Soda.....	2.65
Caustic Soda	4.80
Chloride of Soda.....	.35
Water	91.15
Chromate of Potash.....	.90
Loss, etc.15

Caustic soda should be kept out of boilers. Another case of buying water to get a little alkali.

5. Reddish-brown, very limpid liquid.

Caustic Soda	7.57
Carbonate of Soda.....	2.69
Vegetable Matter (Tannin Extract).....	2.89
Water	86.85

Caustic soda undoubtedly leads to embrittlement, and its indiscriminate use is dangerous. More high-priced water.

6. Very limpid, lemon-yellow, transparent solution.

Water	97.21
Barium Hydroxide	1.61
Barium Chloride16
Loss and undetermined Matter.....	.59

Barium salts should be used only with certain kinds of waters, mainly those carrying large amounts of the sulphates of calcium and magnesium. In other kinds of waters they are useless. Barium hydroxide and barium carbonate are on the market in solid form, and water is usually cheaper at home than shipped a thousand miles or so.

7. Exceedingly thin dark-brown liquid, neutral reaction.

Water	86.13
Carbonate of Soda.....	2.29
Chloride of Soda.....	.68
Sulphate of Soda.....	.16
Organic Matter	10.75

A vegetable extract in very dilute solution, with soda ash to take care of the acidity. The use of tannin has already been discussed. No comment is necessary on the water.

8. Very viscous dirty-gray mixture having a strong odor suggestive of sea-weed or marine growth.

Water	89.12
Carbonate of Soda.....	3.97
Caustic Soda60
Salt	Trace
Organic Matter	6.31

Amount of organic matter too small even if it were of any value. The danger of such organic compounds has been pointed out. Otherwise, a very dilute solution of soda ash. No comment is necessary on the water.

9. White, milk-like emulsion, containing considerable quantity of oil in globules, which separate out on standing.

Water	86.16
Castor Oil	9.92
Free Acid (principally sulphuric).....	2.40
Sulphates (in organic combinations).....	.75
Ash18
Loss and Undetermined Matter.....	.59

Castor oil compounds that are made right may be used under some conditions, but with extreme care. This material contains a free mineral acid, which will render it highly dangerous.

10. Solid material.

Calcium Carbonate	6.04
Tri-Calcium Phosphate	83.71
Iron and Alumina	Trace
Magnesia	Trace
Organic Matter	7.25
Water	2.60
Loss and Undetermined Matter.....	.40

This compound is worthless, being mainly a filler with a small amount of organic matter. Calcium carbonate is the same composition as scale. The tri-calcium phosphate is also insoluble, and hence valueless. As well put a load of dirty rocks in the boiler for all the good it would do. A pure fake.

11. Solid Material.

Tri-Calcium Phosphate	81.70
Iron Phosphate	2.73
Tri-Sodium Phosphate	13.39
Moisture	2.18

The sodium phosphate is the only effective constituent. It can be bought pure, instead of with 85 per cent filler. The remarks under 10 apply here.

12. Dirty-white stick, easily powdered.

Moisture	9.52
Potassium Chromate82
Soap Stone	89.66

An absolute fake. Any other kind of powdered stone would have been as useless.

13. Solid Material.

Tri-Calcium Phosphate	91.32
Moisture and insoluble matter.....	8.62

A nice load of dirt from the garden would have served as well.

14. Reddish-brown powder.

Moisture	5.37
Soluble Organic Matter	2.20
Phosphate of Soda.....	1.12
Insoluble Mineral Matter.....	89.13
Insoluble Organic Matter.....	2.18

More dirt.

15. Coarse, yellowish-white, granular powder.

Soda Ash	72.66
Powdered Soap	27.34

The soda ash is all right in its place, which is generally outside the boiler and in a softening tank. What engineer is fool enough to put soap deliberately into a steam boiler?

16. Salmon-colored Substance.

Moisture	10.66
Insoluble and coloring matter.....	.53
Carbonate of Soda.....	48.83
Caustic Soda	1.85
Chloride of Soda	38.14

Salt does no good and may do harm. Why not buy a good grade of soda ash, at least 95% pure? Of course it may not be salmon-colored, but at a pinch, it might be dyed.

17. Pinkish powder, soluble in water

Fluoride of Soda.....	81.30
Chloride of Soda.....	3.62
Moisture	13.56
Undetermined Matter (principally coloring matter)	1.52

The main constituent is four or five times as expensive as soda-ash, and no more efficient. Aside from the expense, the compound is all right as far as compounds go.

18. Solid Material.

Moisture	7.82
Sodium Chloride	74.76
Sodium Carbonate	15.90
Undetermined Coloring Matter	1.52

Why buy useless salt to get 16 % soda-ash.

19. Solid Material.

Carbonate of Soda.....	2.65
Chloride of Soda.....	9.11
Oil	16.95
Organic Matter (other than oil).....	1.85
Moisture	11.08
Loss and undetermined matter.....	2.17

Loading soda-ash down with a cheap filler is bad enough, but to put oil with it is very much worse. Oil is dangerous in a boiler and is separated from return water as much as possible. This compound gets out of the ridiculous into the dangerous class.

20. Black Mineral Oil.

Mineral Oil	98.97
Oil of Mirbane.....	1.03
Gravity	28.2° Be
Flash Point	410.0° F
Burning Point	470.0° F
Viscosity at 212° F.	104 (Tagliabue)

As a "scale resolvent" this stuff is a failure, but as a source of burned and bagged tubes and pitting, it is a grand success.

WHEN TO USE COMPOUNDS

As to when a boiler compound may be used, or when a water admits of treatment within the boiler, it may be said that whenever a water carries less scaling constituents than the average limit of efficiency of a lime-soda process softening plant (from 50 to 75 parts per million in terms of scale formed) it is admissable to use treatment within the boiler. If a water carries as much as 100 parts per million scaling constituents, it is best to treat outside the boiler.

OBJECTIONS TO COMPOUNDS

(a) *Sludge*.—The idea of treating a water carrying two or three hundred parts per million (ten to twenty grains per gallon) of incrusting solids, or even more than these amounts, with soda

ash in the boiler is ridiculous. Suppose a water supply carries two hundred parts per million of hardness in terms of calcium carbonate, and a boiler uses two thousand gallons of water per day. That means about three pounds of sludge formed in the water every day. Consider how often it will be necessary, not only to blow down but actually to shut down the boiler and wash it out so get rid of this mass of sludge.

(b) *Foaming*.—Not only this, but the boiler is by this very treatment full of suspended matter in the presence of an alkali, and thus is in the very best and most favorable condition for continuous foaming.

(c) *Lack of Definite Amount*.—In most cases the soda ash or other chemical is not added in any definite amount but is simply dumped in according to guess work. If the amount is small, only part of the scaling solids will come out of solution as sludge, and the remainder will form scale as usual, and likely include some of the sludge, and the boiler is little better off, than before. If the amount is too much, foaming is added to other troubles.

(d) *Bad Boiler Practice*.—The theory of this kind of inside treatment is all wrong. It is only a make-shift where the amount of incrusting solids is too small to make ordinary softening methods practicable. There is absolutely no sense in making a sludge tank out of a steam boiler. It is not a chemical reaction tank. It is an apparatus for making the most, the best and the driest steam with the least possible fuel. Such an apparatus deserves a clean and properly softened water supply. Modern boiler practice and soda ash and similar boiler compounds can never be made to agree, where the raw water carries any considerable amount of scaling constituents. Treat the water outside the boiler. The worst feature of these compounds is that the engineer in most cases has no notion of their composition and their effect. They are not sold on analysis, but are recommended generally by an ignorant salesman, who himself is neither chemist nor engineer, and who is consequently privileged to make all manner of guarantees and promises that cannot be kept. Boiler compounds to prevent scaling should never be used until their composition is known and until a

chemist advises as to the correct amount on the basis of analyses of the water. There should always be continuous control. Only if the amount of incrusting solids is very low, is there any reason or excuse for boiler compounds of this class.

MECHANICALLY ACTING COMPOUNDS

In addition to those compounds just discussed whose action is purely chemical, there is another general class of compounds that are supposed to act mechanically on the theory that they will either coat the walls of the boiler so that scale will not adhere, or else that they will permeate the scaling solids as they settle and keep them loose. Most of these substances are vegetable in their composition, such as sea-weed, potato meal, bran and the like, all of them more or less harmful and dangerous. Organic materials of all kinds combine with the sludge, bake into the scale, and burn, causing corrosion. Graphite is thus used, and is especially objectionable. Quite recently a graphite compound was fed into one of the boilers of a local power plant. On cleaning the boiler it was found that instead of loosening the scale, the compound had actually served as a binder. It occurred in alternating layers, which recorded periods of firing and cooling the boiler. Worse than this, on removing the scale, severe pitting was found to have taken place under the scale. Suppose the inside of a boiler could be coated smoothly with graphite. The only practicable way to do this seems to be to mix the graphite with oil and apply it with a brush. Then it would last only an hour or so and do more damage and waste more heat than a thick scale. The idea of dumping loose graphite into a boiler and expecting it to spread uniformly over the boiler surface and cause the scale seeking a resting place to slide off to the mud valves is like waiting for a miracle.

LEGITIMATE COMPOUNDS

There are a few makers of boiler compounds who are going into the matter scientifically as well as legitimately. In the first place, an honest manufacturer will not recommend a treatment that is not the correct one for the particular case in hand. Then the amount to be used will be specified and the method of con-

trolling the dosage will be given. The modern compound business is taking account of real scientific principles in treating boiler waters. The object in an anti-scaling compound is to alter the small amount of scaling solids (since only waters light in incrusting constituents should be treated anywhere but outside the boiler) into a loose, non-crystalline, non-adhering sludge. It has been claimed by reliable chemists that certain organic compounds, such as the sugars derived from tannins in amounts so small as to be safe will aid very much the action of such substances as soda ash. Further, alkaline tannates are regarded by chemists who have conducted extensive experiments on corrosion as being very effective in checking or hindering corrosive tendencies due to galvanic action, by forming interfering compounds and thus lessening ionization. In a very limited degree, emulsions of vegetable oils like castor oil may be used to check foaming. The dosage should never exceed a pint of emulsion carrying 15 per cent of oil to 8,000 to 14,000 gallons of water, and no great amount of this compound should be allowed to collect in the boiler.

Summing up: a great many boiler compounds are not only pure fakes and utterly useless, but absolutely dangerous; those that are of value should only be used when this is the only way of handling the problem; when they are employed, it should only be after a chemist has been consulted and the problem thoroughly gone into by him, and correct control and treatment prescribed. Never buy a boiler compound unless its composition and effects are known, and never put it into a boiler except in definite amounts and with full understanding of its purpose and results. And above all, *never use a compound when the amount of sludge formed is over one hundred parts per million (five or six grains per gallon)*. DO NOT MAKE A SLUDGE TANK OUT OF A BOILER.

2. Preheaters

PREHEATER NOT A SOFTENER

There is a mistaken notion among many engineers that the hardness of a water can be removed in the preheater before it reaches the boiler. *Preheaters alone will not remove hardness.*

The water does not remain in an open feed heater long enough to begin to get rid of the temporary hardness, but just long enough to start the sludge coming out, and to keep the machine clogged. No permanent hardness at all will be removed at the temperature of water boiling under ordinary pressure. In a "live steam heater" (that is one which is closed, and into which instead of exhaust steam, live steam directly from the boiler is admitted under pressure) all the temporary hardness separates, but only a part of the permanent hardness. If this class of hardness is to be removed entirely in the preheater, soda ash has to be employed. Even if both classes of hardness could be gotten out in a feed water heater, it would be bad engineering practice to keep this apparatus jammed up with dirt and sludge. The more space the sludge takes up, the less effective is the heating surface, and the worse work the heater will do. Never rely on the preheater for this service. **THE PREHEATER ALSO IS NOT A SLUDGE TANK.**

CHANGE OF WATER IN PREHEATER

Dr. J. C. Wm. Greth has written a series of very helpful bulletins on water softening problems. We are glad to be able to quote from one of them regarding the mistaken idea that many engineers have that hard water does not have to be treated if a preheater is used, thinking that the scaling constituents will separate there as a sludge. Dr. Greth says:

"There is a popular fallacy as to the efficiency of preheaters as boiler water purifiers. Time is an important factor in the removal of temporary hardness by heat. Following is a practical example: A 1200 h. p. exhaust steam heater of standard make has an interior volume of 144 cu. ft., hot water storage capacity of 480 gallons, or 4000 pounds of water. This allows seven minutes storage. The vertical fill is five feet. One minute is the maximum time of actual heating, or a total time the water is in the heater of eight minutes. In order to effect practical removal of temporary hardness, thirty minutes should be the minimum time of heating. Precipitation by heat is a gradual process. Not enough time is allowed for the removal of temporary hardness in an exhaust steam heater, nor for permanent in a live steam heater. A live steam heater will take out the temporary hardness, but only part of the permanent. The resulting scale is very hard. The feed lines from pre-heaters are frequently badly scaled. Further the danger of corrosion from

soluble magnesium salts is much higher when the carbonates are removed. The apparent reduction of impurities is partly due to dilution by condensed steam. Following shows the actual reduction in a feed water which is passed in turn over a steam condenser, through an open feed water heater, and then through a live steam heater.

	Incrusting Solids in Grains per Gallon
Raw water	41.5
After passing over steam condenser.....	34.0
After passing through open feed water heater..	24.0
After passing through live steam heater.....	17.0

Most of the remaining hardness was permanent, and the carbonates which would tend to prevent corrosion were removed. Consider as another fatal objection to using preheaters as scale removers, the vast amount of scale which would accumulate in a short time. Using the same exhaust steam heater referred to above, there is an interior volume of 144 cubic feet. Of this 58 feet are used for water storage and 70 feet for steam space, the balance being occupied by trays. Suppose it to be fed with well water containing 21 grains incrusting solids, of which from 75% to 80% are temporary hardness. Scale to the amount of 263 pounds will be deposited in the heater every day, or 2.5 cubic feet of scale. The steam space would become solid with scale in 28 days. Suppose a soda-ash solution is fed into a live steam heater of 2000 h. p. with 204 cubic feet steam space, and filter area of 77 square feet. Assume a water is employed of 18 grains temporary hardness as calcium carbonate, and 10 grains permanent hardness on the same terms. The precipitate would amount to 12 pounds of sludge per hour, or 288 pounds every 24 hours. This would occupy 35.5 cubic feet and give a depth on the filter area of 5.5 inches. It would take only a very short time to plug the filter, and make it necessary to use the by-pass, allowing sludge-laden water to run into the boiler."

3. *Water Softeners*

There are two general methods of softening water outside of the boiler: the lime-soda process, and the artificial zeolite process. From both types of water softening apparatus, clear, soft water is supplied to the steam plant. The fundamental principles of construction and operation of the best known types will be discussed.

LIME-SODA PROCESS

It is not necessary to understand the chemistry of the lime-soda process to be able to use it. The following brief summary is given mainly for the benefit of those readers who may wish to know something of the chemistry involved.

(a) *Chemical Reactions.*—Calcium hydroxide, or hydrated lime (in suspension as milk-of-lime) and carbonate of soda, or soda ash (in solution) are the chemicals used. Hydrogen ions (acidity) are removed by conversion to water by the hydroxyl ions. Carbon dioxide is converted to the carbonate ions and water. The bicarbonate ions are changed to carbonate ions and water. Iron, aluminium and magnesium ions combine with the hydroxyl ions to form insoluble hydroxides. The calcium ions, both those already present in the water and those added as lime, are removed in the form of insoluble calcium carbonate. The sodium ions from the added soda ash stay in solution. In other words, the lime removes all the carbon dioxide gas, all the hydrogen, iron, aluminium and magnesium ions, and a part of the calcium ions; the soda ash removes the remaining calcium ions, leaving no incrusting constituents in the water. The relative amount of each chemical needed is roughly proportional to the amount of bicarbonate ions with reference to the other acid ions. A part of the calcium ions are removed by lime, and a part by soda ash, depending on the relative proportion of bicarbonate ions to the remaining acid ions. All magnesium ions require both lime and soda for their removal, since in the process of being precipitated as magnesium hydroxide, equivalent amounts of calcium ions are left in the solution, which must be removed with soda. Waters that are high in chloride ions, and particularly sulphate ions, require considerable amounts of soda and because of their effect on suspended matter, the increased alkali salts give rise to foaming. Some waters, particularly those from gypsum deposits, cannot be successfully softened for this reason. What the engineer wants to know is whether lime-soda will remove hardness, and what are the practical details of the apparatus used.

(b) *Cold Intermittent Process.*—Intermittent softeners were the original type used in the lime-soda process and are still the

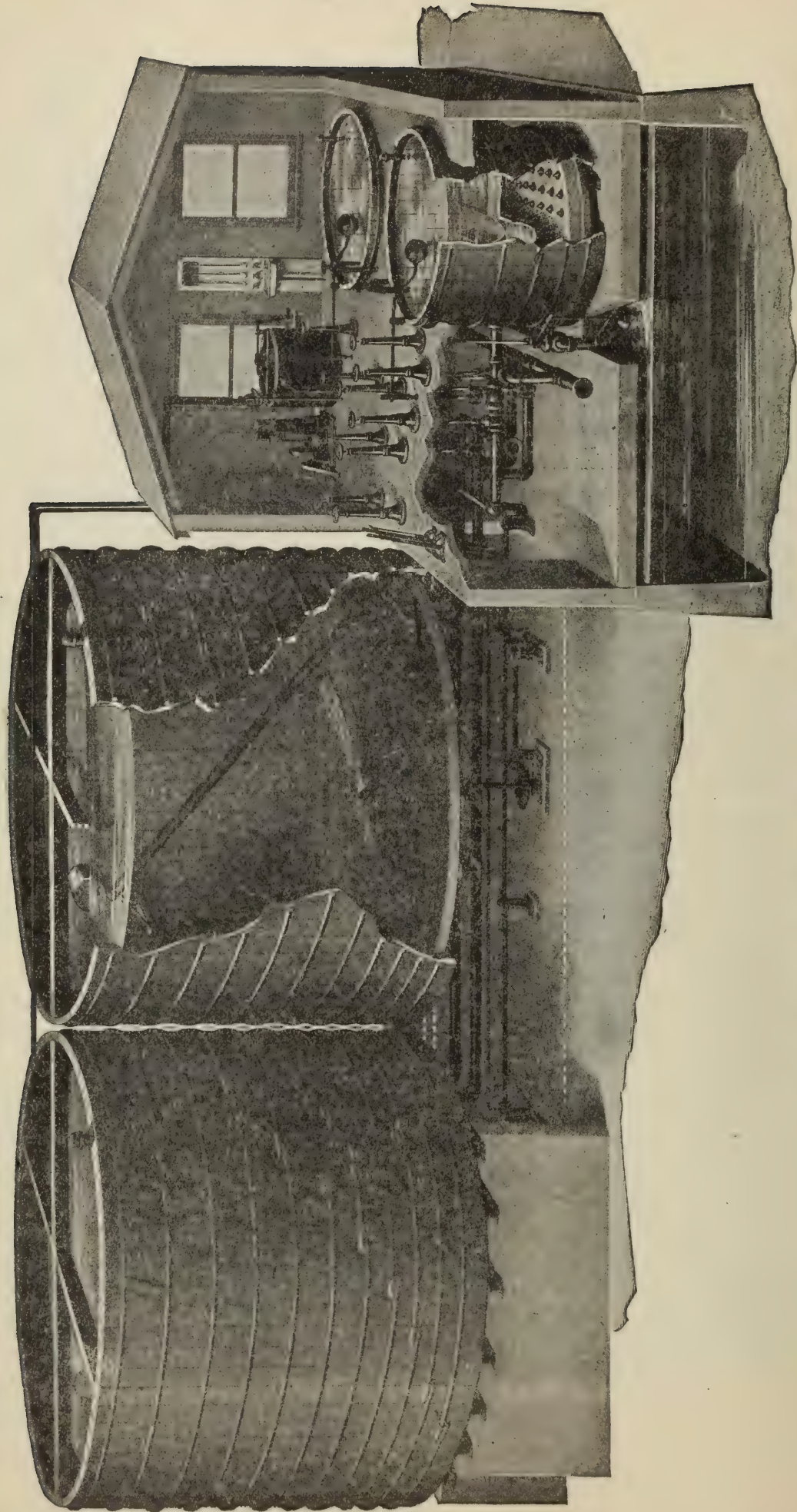


Fig. 6. We-Fu-Go intermittent cold-process lime-soda softener.

prevailing type in smaller installations. The construction of this type of apparatus is very simple. It consists of a tank of the required capacity, fitted with a feed pipe for the raw water, a drain pipe for emptying, and sludge valves on the bottom of the tank for carrying off the insoluble precipitates. Devices for stirring are provided, either revolving paddles or air jets. It is very important that there should be thorough agitation while the chemical reactions are taking place, and all softeners using lime-soda provide for this stirring. There are besides the main tank, small tanks in which the reagents are prepared, and from which they are run into the reaction tank. One make of intermittent softener uses a floating drain pipe (See Figure 6) to remove the treated water, taking the water from near the surface, and thus avoids stirring up the settled sludge. The tank is filled nearly full with raw water, the chemicals added, the contents stirred the required length of time, then allowed to settle until clear. If a test shows the treatment was not correct, either additional chemicals are put in, or more raw water to handle the excess of reagent. In all cases it is necessary to filter the softened water to remove suspended sludge. Intermittent softeners require considerable storage tank capacity for handling sufficient supplies of the treated water.

(c) *Cold Continuous Process*.—Continuous processes are rapidly superseding the intermittent for larger installations. In a continuous, cold process softener, raw water is continually fed into one part of the apparatus, and treated water taken from another part, the water making the complete circuit in not less than four hours. As in all other power plant machinery, there is considerable variety in minor details, but general uniformity in principle. Cross sections are given of some of the more common types of continuous softeners in Figures 6, 7, and 14. These softeners are composed of two main parts, the reaction chamber, and the settling and storage chamber. The reaction chamber is the smaller of the two and is generally contained within the settling and storage chamber. The water is fed into the reaction chamber and mixed thoroughly with the chemicals by vigorous stirring. It passes down and out into the larger portion of the tank, or the settling chamber, in which the water is

amount of chemical solutions fed. Another employs a system of siphons by which a tank, filling through a continuous feed, and emptying with a siphon drain, primes another siphon from a continuously fed chemical solution tank. Still another employs a cone regulating device. A difficulty is always met in keeping these regulators clean and in working order. Every effort is made to keep the chemical solutions from touching any more of the parts of the regulating device than absolutely necessary. These devices are not "fool-proof," but with intelligent care give good service. Continuous processes require no additional storage space, as the water moves without interruption from the source to the boiler.



Fig. 8. Booth water softener. Cold continuous lime-soda process. Fifty thousand gallons per hour. Chicago, Rock Island & Pacific Railway. (View.)

(d) *Hot Continuous Process*.—A still later improvement in the continuous process is the heating of the contents of the reaction tank. By using exhaust steam, the separation of the solids produced can not only be immensely hastened, but made much more complete. Gases are entirely gotten rid of. Furthermore, the sludge particles are larger, the settling is quicker,

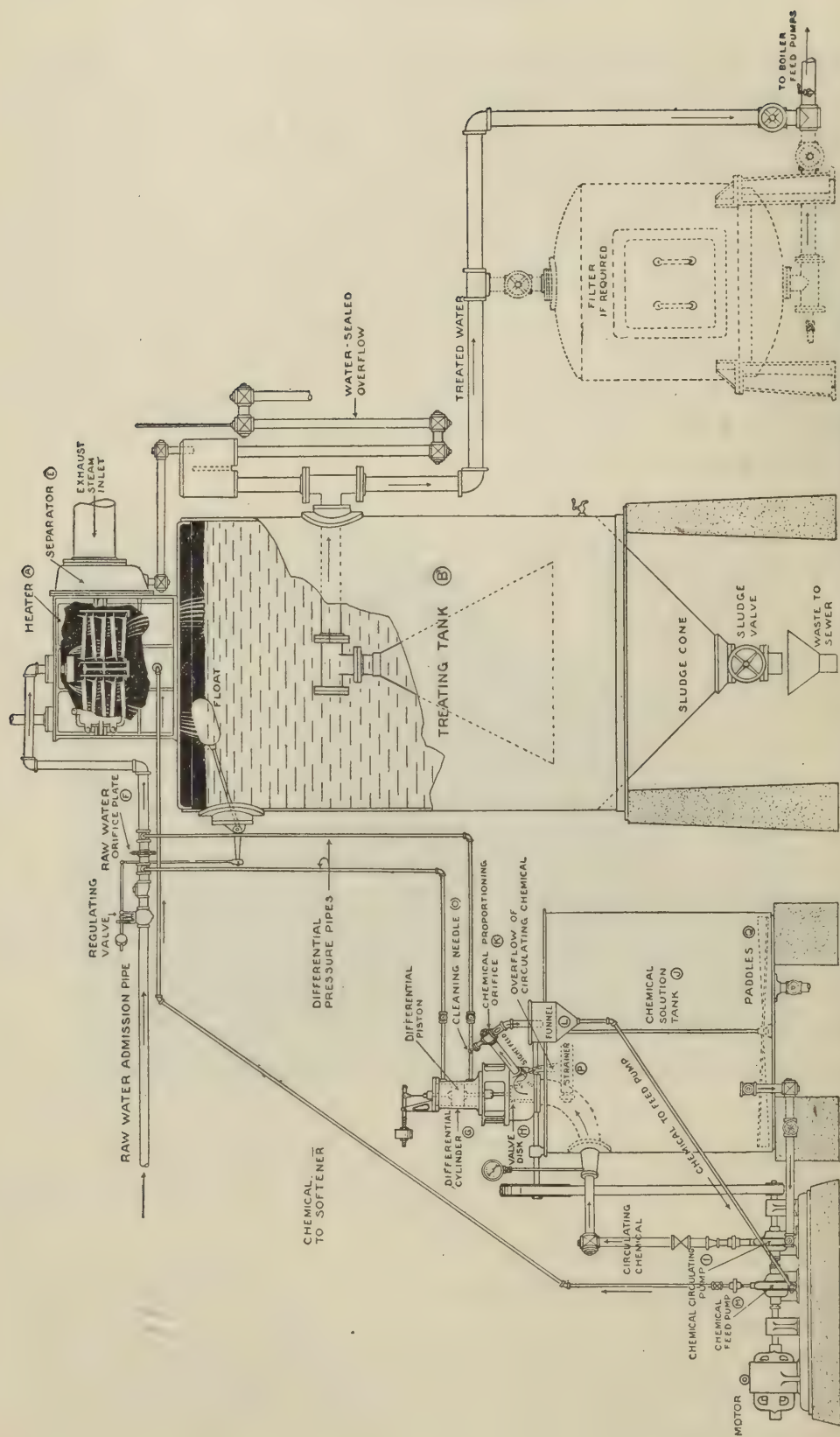
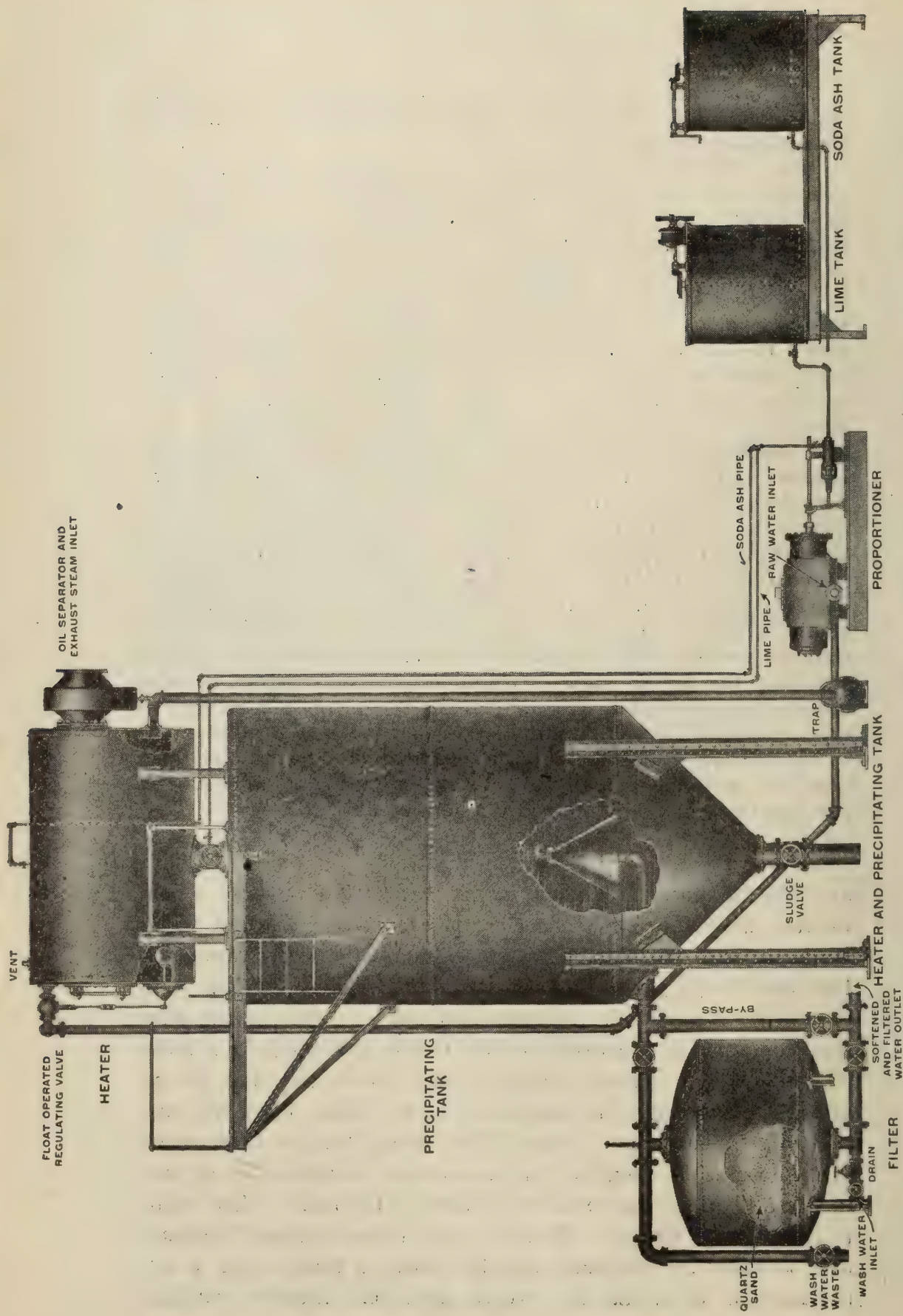


Fig. 9. Sarge-Cochrane hot-process, continuous, lime-soda softener.

The following description of the Sorge-Cochrane hot-process water softener is reproduced through the courtesy of the Harrison Safety Boiler Works:

"This apparatus is designed to take advantage of the fact that chemical reactions are more rapid and complete in hot water than in cold water, and that the resulting precipitates are coarser and settle out more rapidly. The raw water is first heated by means of exhaust steam from pumps, engines or other apparatus to approximately 210° F., or higher, depending upon the back pressure carried. It is then mingled with the softening reagent and drops into a reaction and sedimentation tank, where a large part, and in many cases practically all the sludge settles out and is removed from the conical bottom of the tank by periodic blowing off. The chemicals ordinarily employed are hydrated lime and soda ash. The chemicals are mixed with water in a tank at the ground level, and the mixture is fed into the chemical pump in accurate proportion to the flow of raw water into the softener by means of a differential pressure device similar in principle to a flow meter. The treatment is controlled by varying the amount of reagents per gallon of mixture. Due to the more rapid and complete reaction obtained with hot water, there is little or no after-precipitation of sludge in piping, pumps or boilers, and the latter can ordinarily be operated satisfactorily at moderate or even high overloads without requiring the use of filters. Where filters are required, as with certain kinds of water, and high overloads, or rapid variations of load, or with boilers of certain design, they are installed externally to the softener, and it is recommended that they be installed only after the need has actually arisen, and after taking into account first cost, cost of operation, and the benefits to be gained."

and filtering easier. The cost is no greater than that of a cold process, and if properly handled is even less. The hot water softener takes the place of a preheater. Another advantage is that less sludge gets into the boiler from a water that has been chemically treated hot. A water softened cold still carries some small amounts of incrusting solids, due to incomplete reactions. There is always present a little excess of soda ash, and the reactions being brought to completion in the boiler, there will separate out a carbonate sludge. This sludge begins to separate in the preheater, clogging this apparatus, continues to deposit in the feed pipes, and produces sludge in the boiler. This adds to the foaming danger. To avoid this, in most cases, filters are used between the preheater and the boiler, a thing which is not necessary at all in the hot process, since one filtration suffices.



THE WATER CONSTANT TEMPERATURE WATER SOFTENING SYSTEM

Fig. 10.

CaO PRESENT AS CaSO4 BEFORE TREATMENT

5.56RS. PER GAL.

CaO PRESENT AS CaCO3 AFTER 5 HOURS TREATMENT WITH Na2CO3 AT 50°F.

1.7 GRs. PER GAL.

CaO PRESENT AS CaCO3 AFTER 5 MIN. TREATMENT WITH Na2CO3 AT 200 TO 210°F.

1.16RS. PER GAL.

MgO PRESENT AS MgSO4 BEFORE TREATMENT

4.5 GRs. PER GAL.

MgO PRESENT AS Mg(OH)2 AFTER 5 HOURS TREATMENT WITH Ca(OH)2 AT 50°F.

1.8 GRs. PER GAL.

MgO PRESENT AS Mg(OH)2 AFTER 5 MIN. TREATMENT WITH Ca(OH)2 AT 200 TO 210°F.

.4 GRs. PER GAL.

TABLE OF EQUIVALENTS

1gr. CaO	IS EQUIVALENT TO	179 gr. CaCO3	1gr. MgO	IS EQUIVALENT TO	1.44 gr. Mg(OH)2
1gr. CaO	"	"	1gr. MgO	"	"
		243 gr. CaSO4			2.98 gr. MgSO4

Fig. 11. Effect of heat on amount of scale removal.

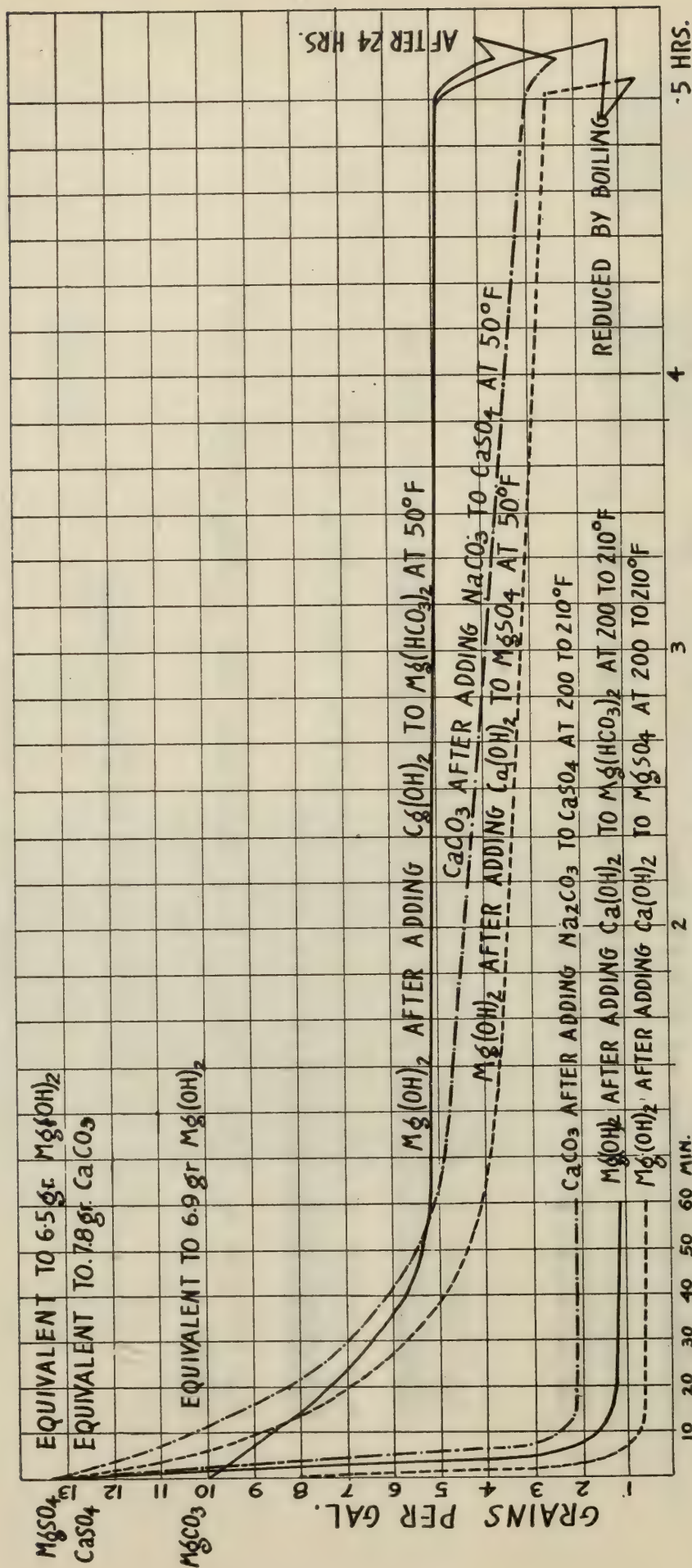


TABLE OF EQUIVALENTS

1 gr. $Mg(OH)_2$ IS EQUIVALENT TO 1.44 gr. $MgCO_3$ 1 gr. $Mg(OH)_2$ IS EQUIVALENT TO 206 gr. $MgSO_4$
1 gr. $CaCO_3$ IS EQUIVALENT TO 1.36 gr. $MgSO_4$

Fig. 12, Effect of heat on time of scale removal,

(c) *Efficiency.*—The relative efficiencies of the different methods of lime-soda treatment, of course, vary with the care that is bestowed upon them and the attention that is given to the changes that take place from time to time in the mineral content of the water. A closely controlled cold intermittent softener should not leave over 50 parts per million (three grains per gallon) of calcium and magnesium salts in solution; the average cold continuous process allows 85 parts per million (five grains per gallon) as a maximum, and often does better than this; a hot process will average from 25 to 35 parts per million (one and one-half to two grains per gallon) and some times less, with the special advantage of removing the magnesia practically completely. The choice of a softener depends solely on all the conditions in each plant. There are thousands of lime-soda softeners in operation all over the world. In the United States there are a number of standard makes of apparatus that have proven successful. A reputable manufacturer will not attempt any installation unless he knows it will fulfil the needs and requirements. No softener should be put in until all the facts of the water supply and the entire plant are known.

ARTIFICIAL ZEOLITE OR "PERMUTIT" PROCESS

While there is no secrecy as to the composition of the substance which brings about the removal of the scaling constituents in the Permutit or "artificial zeolite" process the method and all the patents on the plant and softening chemicals are controlled by an American syndicate.

(a) *Chemical Reactions of "Permutit."*—Permutit is an artificial zeolite, made by fusing together felspar, kaolin, pearl ash and soda in definite proportions and treating the resulting substance with water to bring about hydration and to wash out the soluble silicates. The process of manufacture is not as simple as this description sounds, and only long experience of the makers, and rigid control of the process of manufacture enables them to make a uniformly satisfactory working product. Permutit is a granular or flaky substance with a pearl-like lustre, and is very porous. Chemically it may be denominated as a hydrated sodium-aluminium silicate, $H_{12}Al_2Na_2Si_2O_{14}$, or accord-

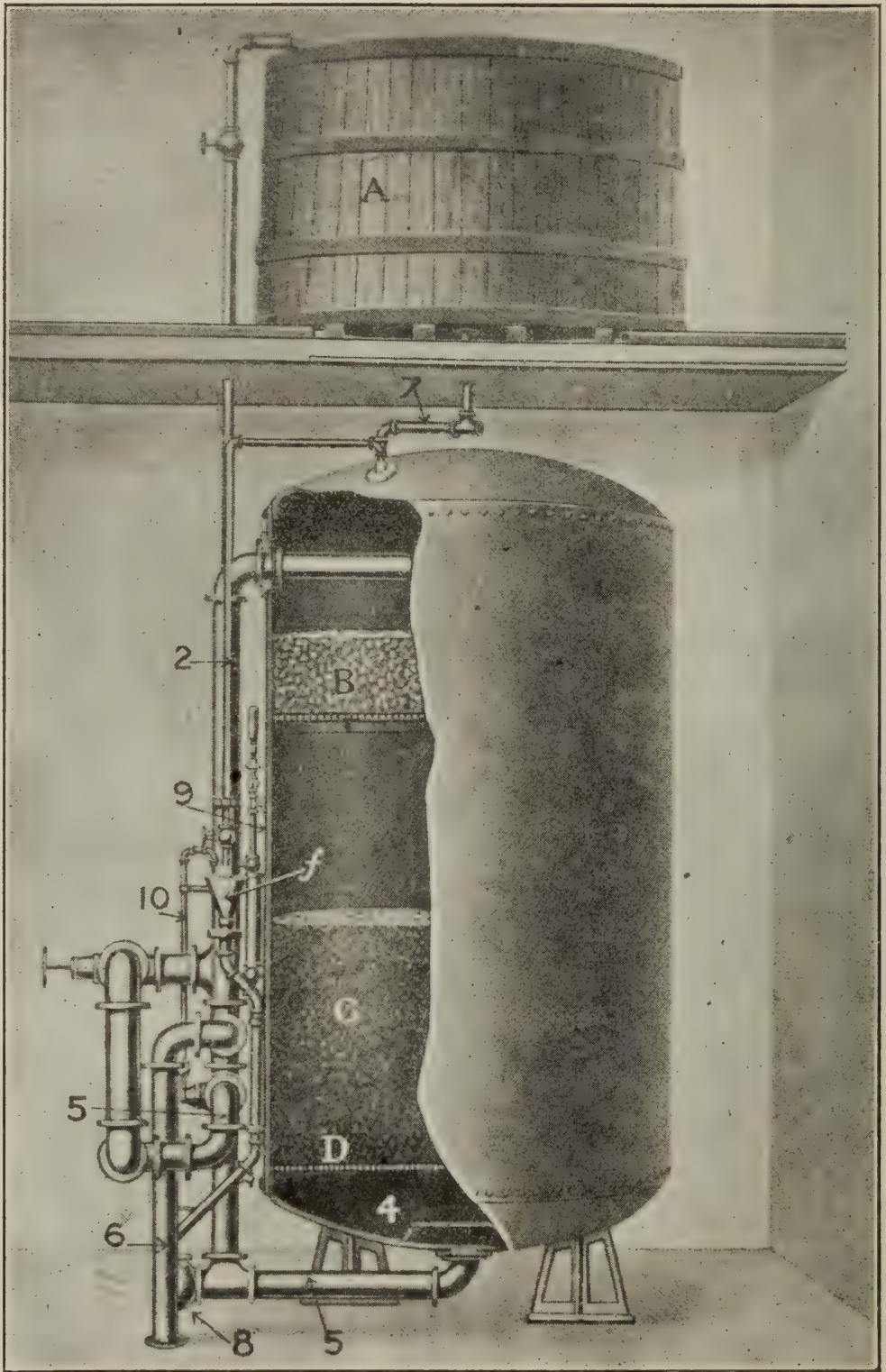


Fig. 13. The Permutit water softening system.

ing to the mineralogical formula, Na_2O , $6\text{H}_2\text{O}$, Al_2O_3 , 2SiO_2 . When water containing salts of calcium and magnesium is passed through a bed of this zeolite, there is a replacement of the sodium of the silicate by the calcium and magnesium. Instead of hard water, the resulting product is a solution of alkali salts, the sodium that is due to the Permutit being present in proportion to the combining weights of the calcium and magnesium replaced. The acid ions, of course, are unchanged. There is simply an exchange or "swap" between the calcium and magnesium, and the sodium.

(b) *Construction of Softener.*—The mechanical details are very simple. The softener consists of a cylinder filled in the central portion for about two-thirds of its total length with the Permutit, held in by perforated plates. Above this is a layer of marble to react with the carbon dioxide dissolved in the water. There is a clear space above and below the softening material. The cylinder may be open above for gravity feed, or closed for pressure feed. The fittings are ordinary galvanized iron pipes with the usual type of valves.

(c) *Method of Operation.*—The water passes through the apparatus slowly, at the rate of 10 to 15 feet per hour. Occasionally the flow of water is reversed and the bed of zeolite thoroughly torn up and stirred to prevent packing and the formation of channels. In the course of time, depending on the amount of water that has passed and on its hardness, the zeolite bed begins to fall off in efficiency, and minute amounts of calcium and magnesium appear in the water at the outlet. Then the water supply is cut off from the softener and in the case where a continuous supply of water is demanded, this is connected to a fresh unit. The partially exhausted softening material is regenerated by the use of a strong solution of common salt—in other words the softening process is reversed. By virtue of the great excess of sodium ions present in this strong solution of sodium chloride, the calcium and magnesium present in the spent softening material are replaced by the sodium, the original sodium—aluminium silicate of the same composition as this original zeolite being reformed. After this strong salt solution has been in the apparatus for some hours, it is drained

out and run into the sewer. (In manufacturing centers or at chemical plants, it might be economically used as a source of chlorine in the making of bleaching powder or liquid chlorine. In small plants, however, it is a waste product.) The zeolite bed is then washed to remove traces of the strong salt solution, and is ready once more for use. These operations produce but a very slight actual loss of the Permutit, and the substance is capable of hundreds of regenerations. A maximum of five per cent per year is considered to be the loss of softening material.

(d) *Efficiency.*—Through the courtesy of The Permutit Company, a small household apparatus was placed in the Chemical Laboratory of the University of Texas. Its rated capacity on the basis of analyses of the city water supply for ten day intervals for one year was 150 to 200 gallons before regeneration was considered necessary. The water passed through was checked up by a meter, showing both the flow in gallons and the rate of flow per minute. Samples were taken at intervals. Within the rated capacity at the given rate, no trace of calcium or magnesium ions could be found in the water unless considerable amounts were concentrated for test. This softener was purposely overtaxed and it was found that only after some 600 gallons had passed through did the hardness reach the lowest figure obtainable with cold lime-soda treatment. Several thousand gallons of hard water from the Austin city water supply have been put through the softener and it has been regenerated repeatedly; and from all tests, it appears as efficient as ever. On the basis of a water giving 3.1 pounds of scale per thousand gallons, 5.5 pounds of salt were required to regenerate this small apparatus every 200 gallons, or a rate of 27.5 pounds per thousand gallons. A small softener necessarily requires much more salt in proportion than a large one. On the basis of this water supply, if the Permutit process alone is used, a regulation size softener should not use over 16 pounds salt per thousand gallons.

(e) *Control.*—The only control necessary on a system of this kind is a test with a soap solution. The first failure to give a rich lather (by the addition of a few drops of soap solution to a sample of the water and shaking it in a glass stoppered bottle)

is a signal that the unit is to be shut down and regeneration started.

(f) *Advantages and Disadvantages.*—Aside from mechanical considerations the Permutit softener affords an excellent method of water purification in that it produces a water of zero hardness, a thing essential for instance in textile industries. There is no control necessary, or in other words the process is "fool-proof." There is no problem of sludge disposal since there is no sludge. A disadvantage of the process when used with water high in temporary hardness is the large amount of sodium salts put into the water. In the lime-soda process, the lime put in to remove magnesium and calcium is not itself retained in the water, but comes out in the sludge. In other words, the lime takes out part of the hardness and puts nothing into the solution; but the Permutit filter puts into the water an amount of sodium, corresponding to all the salts removed. If the bicarbonates are high the softened water will contain excessive amounts of sodium carbonate. For this reason with a water of high temporary hardness, it is advantageous to use a tank softener with lime alone, and then remove the residual hardness, the presence of which is to be avoided for reasons previously given under the heads of corrosion and foaming, with Permutit. In fact this is what is usually done in such cases.

LIME-PERMUTIT PROCESS

The lime-Permutit process consists of either an intermittent or continuous tank installation connected through a filter, with a Permutit softener. Only milk-of-lime is fed into the reaction tank, the work of the soda being done by the Permutit. The cost of the lime is of course the same in this process as in the lime-soda method. The variation is in the difference between the cost of soda for direct treatment and salt for regeneration of the zeolite bed. It is stated by the manufacturers that the amount of salt needed for regeneration after removing non-carbonate hardness is somewhere between three and a half and four times that of soda for the same purpose. As pointed out, the Permutit gives complete removal of all hardness, which is impossible even in the best lime-soda softeners. It not only

corrects any mistake in the lime treatment by removing residual calcium and magnesium, but it cleans out all permanent hardness, and leaves a water of "zero" hardness. A filter is necessary on all waters carrying suspended matter, before the water is fed into the Permutit softener. But practically all lime-soda processes employ filters for the treated water, so that item makes no difference between the two. With lime-Permutit softened water, foaming is less likely owing to the absence of suspended matter. Water softened with Permutit alone will carry sodium carbonate in proportion to the amount of temporary hardness, and may cause some foaming, depending on boiler conditions and construction. Since there is no suspended matter at all in water so treated, foaming is not likely with reasonable concentration in the boiler. For the great majority of Texas waters, which carry a considerable amount of bicarbonate or temporary hardness, the lime-Permutit process is much less expensive and more satisfactory than the Permutit process alone.

IRON AND MANGANESE REMOVAL WITH PERMUTIT

Another Permutit apparatus of the same mechanical design, but with a different chemical filler is made to remove iron and manganese salts from water. The chemical principles are not the same, the action being wholly a matter of oxidation. Comparatively few Texas waters carry iron or manganese in notable quantities, and for boiler purposes, these substances would be sufficiently removed by the lime treatment.

4. *Filters*

Although mentioned at different times in the foregoing pages, no special emphasis has been laid as yet in this bulletin on the matter of filtration, since it was thought to be so important as to constitute a special topic. It is highly essential that the water that enters a boiler should not only be *soft* but that it should be *clean*.

MUD REMOVAL

A water which is originally soft, but which carries any amount of suspended and colloidal matter will cause all manner of foaming unless it is filtered. Sometimes it is necessary to use a coag-

ulant to settle fine suspensions. Coagulants should be avoided as far as possible, and when used, the amount should be very small. A mere trace of alum will clear an almost unbelievable amount of muddy water. An excess only means waste and great danger of corrosion in the boiler. When water is treated by coagulants, it is absolutely necessary that it should be maintained in alkaline condition. In general, coagulants are not a safe proposition, and there must be close chemical control in their use. It is not necessary to filter water *before* treatment by the lime-soda process. The chemicals in the reaction tank will serve to some extent as coagulants, and the remaining suspended matter will be removed by the filter, as the treated water flows from the softener. Filters, however, must be used in connection with the Permutit system, before water that has even a very small amount of mud or vegetable matter is fed into the softener. If muddy water is used, the grains of the zeolite are coated, and their chemical action stops. The Permutit apparatus is not a filter at all, but a softener, and requires filtered water. As has been stated, there is no sludge from a Permutit softener, and only the filter ahead of the apparatus is necessary.

SLUDGE REMOVAL

Practically all water softeners are too small, and do not allow sufficient time or space for complete reaction and settling. For that reason the softened water from such softeners carries some sludge. This sludge must be removed by filtration. In fact most water softening systems are constructed to work in connection with filters, and their manufacturers will not guarantee their successful operation without filters. Most of the foaming troubles from softened water are caused by the presence of sludge. No process of water softening is satisfactory or efficient unless the amount of suspended matter is reduced to a minimum. This is most surely and safely accomplished by filtration. In case there is any marked separation of sludge in the preheater, which is often the case where a cold lime-soda process is employed, a small, well-insulated filter should be installed between the preheater and the boiler.

TYPE OF FILTER

Engineers are very generally agreed that the most satisfactory type of filter is the sand or quartz filter with a down flow of the water. This is the most common type, and its efficiency is a matter of record. Excelsior or hay as a filtering medium is not so safe or satisfactory. Filters are not expensive either in original cost or maintenance cost, and only the type which is of proven efficiency should be used.

Summing up! Muddy water, even if it is soft must be filtered. Coagulants are not entirely safe and should be avoided unless water cannot be cleared without them. Hard waters must be softened, and the sludge that remains in suspension must be removed by a filter. The filter must be of a type that is of proven efficiency, preferably the sand filter with down-flow. It is false economy to install a softener and leave out the filter. Filters are necessary in handling either muddy water or treated water that carries suspended sludge.

DANGER OF INCORRECT FILTRATION AND COAGULANTS

A successful maker of water softeners has given these two instances in proof of the necessity for filtration and the danger in the indiscriminate use of coagulants to help out a poor filter.

"A central station, lighting, power and heating plant, capacity of softener 15,000 gallons an hour, cold continuous, type of filter: up-flow through excelsior. Results: trouble from sludge; filled up the flow meters, the water regulating valves, and the superheaters; foaming occurred; blading was stripped out of a 5000 K. W. turbine; cost of reblading \$5000; complained to manufacturers who recommended the use of a coagulant costing \$275 per annum; sulphuric acid released by coagulant ruined four 350 h. p. water tube boilers; boiler inspectors condemned them; company installed new boilers at a cost of \$16,000; five other boilers so seriously damaged that they cannot be operated two years more. Lesson: Always filter the water from a softener, and never use a coagulant in a water used for boiler feed.

"A large chemical plant, capacity of softener 16,000 gallons an hour, cold continuous, type of filter: up-flow through excelsior. In three years foaming, burning tubes, stopping up of auxiliaries has caused an expense of \$15,000. Company is now spending \$12,500 to install filters to remove sludge. Steel plate is now very high. Softener originally cost \$6,500. Was not the failure to install filters originally a crime?"

While we are not prepared to go quite as far in condemning the use of coagulants absolutely, it is imperative that the danger from their use be recognized, and continual care taken to keep the water alkaline.

CHAPTER THREE

COST, CONSTRUCTION AND OPERATION OF WATER SOFTENERS

Having been convinced of the cost and danger of bad water, the manufacturer naturally asks these two questions: "What will it cost to install and operate a water softener?"; and "Will a water softener show a reasonable profit on the investment?" In this chapter, the first question will be discussed, and all information given that it is possible to give in a general way. The next chapter will take up results.

1. *Cost of Standard Patented Water Softeners*

No fair estimate can be made on the cost of installing a water softening system until full information covering the individual needs and requirements of each plant is obtained. Hence in this discussion only the most general figures are given in order that steam power users may gain some sort of an idea of the cost of a water softening plant. It should be kept in mind that, owing to war conditions, structural materials are very high, and any estimate must take into account these abnormal conditions.

VARIATION OF COST WITH SIZE

It is especially true in water softening plants that the smaller the installation, the higher the cost. With very small installations, most water softener manufacturers say frankly that it does not pay to install a patented softener. The increased efficiency over a simple, home-constructed, tank softener does not counterbalance the higher cost of installation in the case of the smaller size softeners. For this reason, plans and estimates for small softeners that can be constructed on the ground are given in a later section.

Cost Quotations: Following are a few quotations given by leading water softening manufacturers on plants of various capacities. (Several firms preferred not to make any definite statements, due to abnormal war prices of materials.)

Capacity per Hour	Total Cost	Cost per 1000 gallons
500 gallons	\$ 1,200 to \$2,000	\$2,400 to \$4,000
1,000 gallons	1,500 to 2,500	1,500 to 2,500
5,000 gallons	3,250 to 6,500	650 to 1,300
8,000 gallons	6,000	750 (one estimate)
25,000 gallons	10,500	420 (one estimate)

From the above figures it is evident that under present conditions for any plant using less than 1000 gallons per hour, the cost of a water softening system as manufactured by power plant supply companies seems to be prohibitive.

QUOTATIONS FOR EACH INDIVIDUAL CASE

The reader is advised, however, not to take these figures as anything more than general approximations. Before installing any kind of system, it is advisable to give the full facts of the plant and water supply to several reliable companies for bids and estimates. An honest manufacturer of water softeners will not sell a softener that does not pay a reasonable return on the investment. Most manufacturers make this as a definite statement: "Our softeners are not for sale until we can prove to you that they will pay." It costs nothing to investigate the relative cost of various makers.

MUNICIPAL PLANTS

As the size of the installation increases, the unit cost comes down, until for very large installations and municipal plants, the unit cost is as low as one-tenth the figure given for a small plant. Where the amount of hardness is sufficiently low to make the cost of chemicals a comparatively small item per unit amount of water, large softening plants handling the entire water supply of a city are feasible propositions. A notable example of a small municipal plant is that of Owensboro, Ky., where something over 1,000,000 gallons of water are treated daily. The total cost of the entire installation was less than \$30,000. At Me-

Keesport, Pa., 10,000,000 gallons daily are treated for the use of the city, and the relative cost of this plant is still less than the one of one-tenth capacity. In such cases, the cost of chemicals is the important consideration, the original installation being only a small part of the total cost on a long time basis.

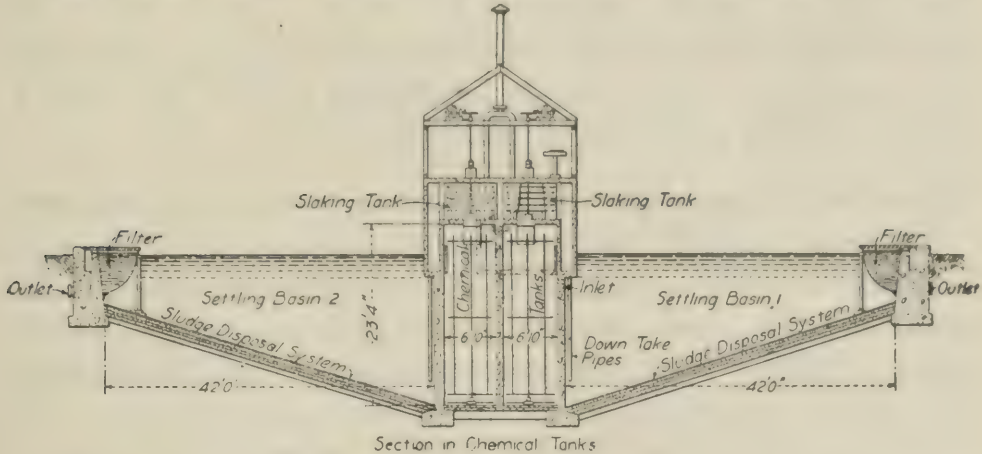


Fig. 14: Booth water softener. Cold, continuous, lime-soda process. Municipal plant, Owensboro, Ky. (Plan.)

2. Cost of Home-Constructed Softening Plants.

LIMITED TO SMALL INTERMITTENT PLANTS

For water softening plants of any considerable size, home construction is neither economical in first cost or in up-keep. Intermittent systems are more expensive both to build and to operate than continuous systems. Where space is an item, as in cities, this also counts against the intermittent method, since a continuous softener occupies much less ground space per unit capacity. It is not possible for any one not an expert in the construction of water softening plants to devise a chemical proportioner. The various successful types of chemical feeding devices are completely covered by patents. This is after all the key to a continuous process, a successful and simple chemical proportioner. Heating the contents of an intermittent softener is not convenient or profitable. The hot process is used only by continuous plants, and these can not be successfully constructed except by an expert water softening engineer.

Hence home-construction is confined to small capacity intermittent plants. Admitting that such plants are less convenient, less flexible, and more expensive to operate, it seems that under present conditions this is about the only way in which water softening can be done by small power plants. It is also often true that an engineer prefers to try out on a small scale with comparatively inexpensive installation the whole problem of water softening, with a view to purchasing at some later time a water softening plant of standard type.

VALUE AND LIMITATIONS OF HOME-CONSTRUCTED PLANTS

For these reasons, some suggestions are given as to the construction of a small, intermittent, cold process softener with concrete reaction and storage tanks. It is not claimed that a softener of this kind will give anything like the satisfaction that will be given by a standard make, continuous softener. But from practical experience with a home-constructed softener of this general type, it is known absolutely that reasonable results can be obtained. Scaling can be reduced to a negligible amount, corrosion entirely stopped, and savings in fuel and labor effected that will pay large returns on the investment.

GENERAL PLAN OF HOME-CONSTRUCTED SOFTENER

The softener proper consists of a tank of cypress or reinforced concrete. Flush with the bottom of the tank there opens a pipe with a valve, which takes off the sludge when the tank is cleaned. Another pipe projects through the bottom eight or ten inches, and is connected through a valve with a standard quartz or sand filter. The feed pipe for the raw water comes up on the outside of the tank. The stirring device here consists of a branching perforated pipe for compressed air or steam. Other devices, such as paddles driven by a water-wheel using the inflow of the water, may be employed, but the use of compressed air has been found to be so cheap, convenient and satisfactory, that no other devices have been studied. For a small plant, sound, heavy barrels make satisfactory tanks in which to prepare the solutions of the chemicals to be used. From the filter the water runs into a storage tank of convenient capacity. With all intermittent systems it is necessary to have a storage

tank of some sort. It is possible to operate with two or more tanks, drawing the water from one while the softening and settling process goes on in another. A storage tank is cheaper and does away with the danger of having to use raw water in case of a temporary shut down of the softener.

CONSTRUCTION DETAILS OF A REINFORCED CONCRETE TANK SOFTENER

(a) *Size and Capacity of Reaction Tank.*—These plans call for a tank of 10,000 gallons holding capacity, which is a convenient unit size for an intermittent softener. The tank should have at the base an inside diameter of 15 feet if circular, or should measure 13 feet each way, if rectangular. The inside depth in either case should be 9 feet. This will allow about one foot margin above the surface of the water if 10,000 gallons of water are run into the tank. This permits adding as much as 1000 gallons more in order to correct a mistake in treatment as determined by tests on the treated water. (A depth gauge worked out in 100 gallon units is very convenient.) The walls should not be less than eight inches thick and the bottom from six to eight inches thick.

(b) *Reinforcing.*—The same reinforcing may be used for either circular or rectangular tanks. The reinforcing should consist of one-half inch round steel rods of a length sufficient to reach from top to bottom of the tank set vertically five inches from center to center with at least three-fourth inch clearance from the inside surface. These vertical rods should be bent ten inches from the bottom at an angle of 45 degrees, the slanting portion pointing inward. Instead of one-half inch round rods five inches from center to center, three-fourth inch round rods eleven inches from center to center may be used for the vertical reinforcing. The horizontal reinforcing should be of one-fourth inch round steel rods placed 18 inches from center to center, and fastened at each intersection. The bottom can best be reinforced by the use of wire mesh of the size usually employed in this kind of work. The wire should be fastened to the vertical reinforcing rods, and should dip from points four feet from each wall to within one inch of the bottom of the floor slab. It is assumed that this tank is to rest on the ground.

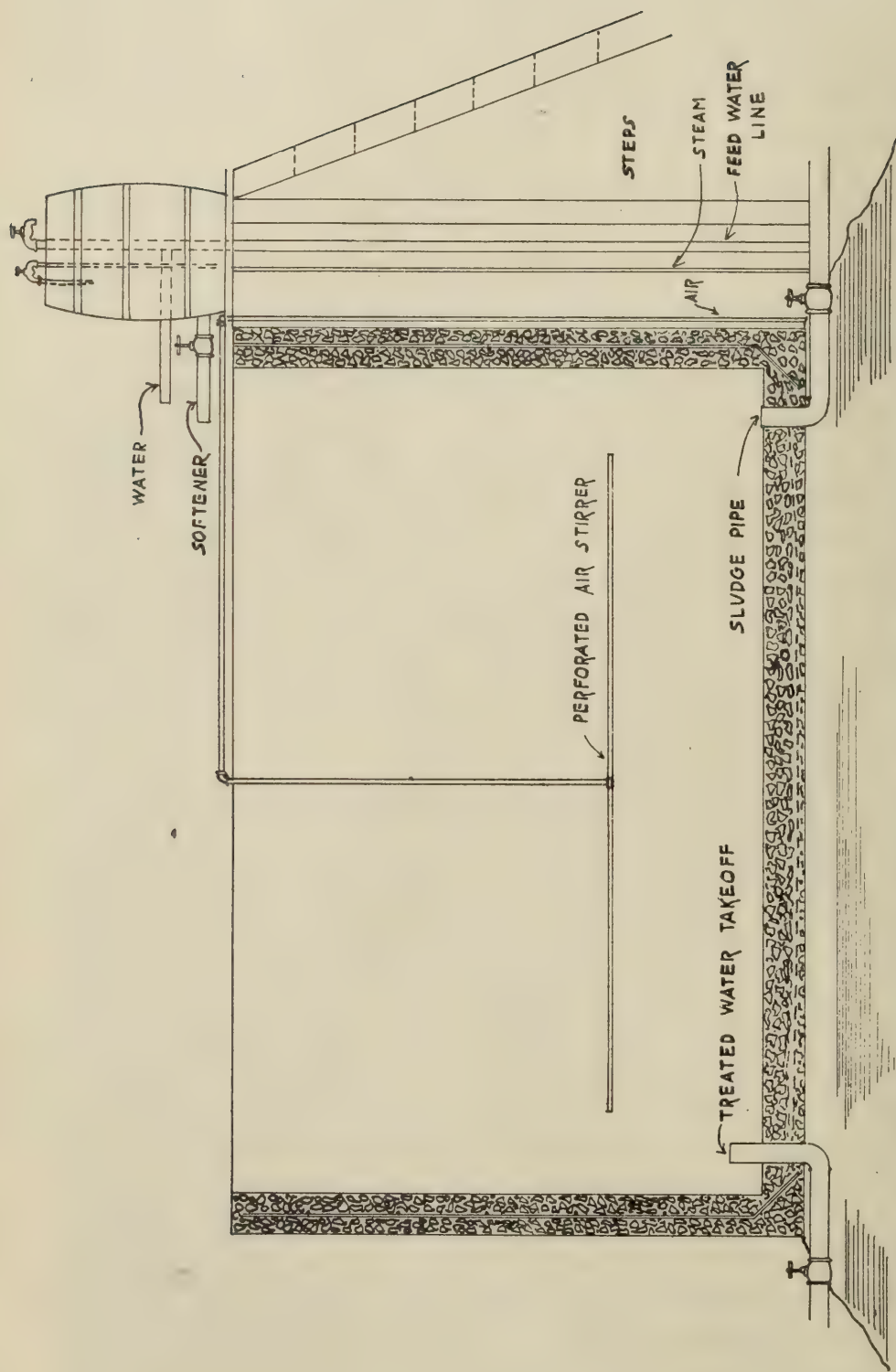


Fig. 15. Home-constructed concrete water softener. Cold, intermittent, lime-soda process.
(Plan of treating tank.)

(c) *Concrete Mix and Waterproofing.*—The concrete should be a 1:2:4 mix, at a mushy consistency, using only enough water to handle the mixture easily. It should require some tamping and spading to flush the water to the surface when placed in the forms. When inside forms are removed the inside of the tank should be well grouted and surfaced like a sidewalk. To this surfacing mixture, should be added 10 per cent by weight (of the cement) of well slaked lime or some standard waterproofing material, in amount recommended by the manufacturer. If the inside is not to be surfaced, it will be necessary to add this water proofing material to the concrete of tank walls and base as it is made up. If possible, the whole tank should be poured at one time. In case there is an intermission of as much as a day in pouring different parts of the tank, all joint surfaces should be thoroughly cleaned with a wire brush and plastered with neat cement just before pouring additional portions. Otherwise, there will surely be leaks at the joints.

(d) *Storage Tank.*—This is most conveniently set in the ground so that there may be a gravity flow to it from the softening tank through the filter. The details of construction are the same here as for the reaction tank, with the exception that the vertical reinforcing should be next to the outside rather than the inside wall. Its capacity should be as much as twice that of the softening tank so as to provide for all emergencies.

(e) *Cost of Construction of Concrete Softening and Storage Tanks.*

The materials, reinforcing steel and wire, and the labor for making a 10,000 gallon concrete tank of the above size will cost, at present prices, approximately \$275.00. For a storage tank that is set in the ground, the cost of excavation will have to be added. If the excavation is mainly in earth, the cost will be from \$30 to \$40, if in rock about twice this amount. In the case of rock, however, the extra cost of excavation would be partly counterbalanced by the elimination of the reinforcing in the base and the outside forms. A plant consisting of one 10,000 gallon softening tank above the ground and one 10,000 gallon storage tank set in the ground, would cost about \$650 to construct.

The pipes, valves and fittings will amount to approximately \$70, and \$30 should care for the labor of installation. A total of \$750 should easily cover a complete softening and storage plant of 30,000 gallons daily capacity.

(f) *Pipe and Fittings for the Softener.*

Following is a list of the fittings necessary for the softening tank shown in Figure.

- 2 ells 4".
- 1 nipple 4x18".
- 1 nipple 4x12".
- 2 pc. 4" black pipe 4'.
- 2 globe valves 4".
- 1 pc. 2" black pipe 10'.
- 1 tee 2".
- 1 pc. 2" black pipe 2'.
- 3 globe valves 2".
- 1 bushing 2x $\frac{3}{4}$ ".
- 1 pc. $\frac{3}{4}$ " black pipe 3'.
- 1 hose bib $\frac{3}{4}$ ".
- 1 pc. $\frac{3}{4}$ " black pipe 14'.
- 2 angle valves $\frac{3}{4}$ ".
- 2 close nipples $\frac{3}{4}$ ".
- 3 ells $\frac{3}{4}$ ".
- 1 pc. $\frac{3}{4}$ " black pipe 2'.
- 1 tee $\frac{3}{4}$ ".
- 1 pc. $\frac{3}{4}$ " black pipe 3'.
- 2 pc. 2" black pipe 2'.
- 4 lock nuts 2".
- 2 nipples 2x12".
- 1 pc. $\frac{3}{4}$ " black pipe 10'.
- 2 pc. $\frac{3}{4}$ " black pipe 7'.
- 2 ells $\frac{3}{4}$ ".
- 1 cross $\frac{3}{4}$ ".
- 1 tee $\frac{3}{4}$ ".
- 1 close nipple $\frac{3}{4}$ ".
- 4 bushings $\frac{3}{4}$ " to $\frac{3}{8}$ ".
- 4 pc. $\frac{3}{8}$ " black pipe 6' (each perforated at 1' intervals with 1-16" holes).
- 4 $\frac{3}{8}$ " plugs.

3. *Cost of Chemicals*

The amount of lime and soda ash used by any type of softener of standard design is approximately the same for a given water. Experience has shown that in a home-constructed intermittent

softener of the type given above, the efficiency of the lime is somewhat less, increasing the cost of this chemical in some cases as high as 10 per cent to 20 per cent. The amount of salt necessary to regenerate a Permutit softener is from three and one-half to four times the amount of soda ash necessary to treat the same water. The cost of lime for a lime-Permutit system is of course the same as for a lime-soda system.

CALCULATION OF AMOUNT OF CHEMICALS NEEDED FROM ANALYSIS OF THE WATER

The amount of lime and soda necessary to soften a given water can be readily calculated from an analysis of the water. The following formulas of Stabler have been found very convenient and accurate.

$$\text{Lime required} = .00931 \text{ Fe} + .0288 \text{ Al} + .0214 \text{ Mg} + .258 \text{ H} + .00426 \text{ HCO}_3 + .0118 \text{ CO}_2 \text{ (gas)}$$

$$\text{Soda ash required} = .0167 \text{ Fe} + .0515 \text{ Al} + .0232 \text{ Ca} + .0382 \text{ Mg} + .462 \text{ H} - .0155 \text{ CO}_3 - .00763 \text{ HCO}_3$$

Given the following analysis, and employing the Stabler formulas. Let us calculate the amount of lime and soda ash necessary to soften this water. (These formulas assume the lime to be lump lime or calcium oxide and of 90 per cent efficiency; the soda ash to be 95 per cent efficiency.)

	Parts per Million
Calcium	138
Magnesium	29
Sodium	69
Carbonates	12
Bicarbonates	290
Sulphates	198
Chlorides	106

Lime required:

$$\begin{aligned} .0214 \times 29 \text{ (Magnesium)} &= .62 \\ .00426 \times 290 \text{ (Bicarbonates)} &= 1.24 \end{aligned}$$

$$1.86 \text{ lbs. 90\% lump lime per 1000 gals.}$$

(To convert lump lime to hydrated lime—CaO to Ca(OH)₂, multiply by 1.32. $1.86 \times 1.32 = 2.46$ pounds 90 per cent hydrated lime per 1000 gallons.)

With lump lime at one-half cent per pound the cost per thousand gallons for the lime would be 0.93 cents.

Soda ash required:

$$\begin{array}{rcl}
 .0232 \times 138 \text{ (Calcium)} & = & 3.20 \\
 .0382 \times 29 \text{ (Magnesium)} & = & 1.11 \\
 \hline
 & & 4.31 \\
 .00763 \times 290 \text{ (Bicarbonates)} & = & 2.21 \\
 \hline
 & & 2.10 \text{ pounds 95\% soda-ash per thousand gallons.}
 \end{array}$$

With soda ash at three cents per pound the cost per thousand gallons for this chemical would be 6.3 cents. The total cost for both chemicals would be 7.23 cents per thousand gallons.

Since the amount of dissolved solids in practically any water supply varies according to the season, it would be necessary to allow for a variation in cost of chemicals from 6 cents to 9 cents per thousand gallons at the prices given.

When an analysis is given in hypothetical combinations, the amount of chemicals necessary to change or remove each scaling salt may be calculated from the analysis. Different methods of calculation give varying results, but these are well within the variation limits of the seasonal changes.

From the above analysis calculated in combined form, take all the scaling ingredients as follows:

Calcium Sulphate	119
Calcium Bicarbonate	385
Magnesium Sulphate	143

Using the factors from the table given below, these results are obtained.

(The amounts of each salt being in parts per million, it will be necessary to convert to pounds per thousand gallons by multiplying each result by .00833.)

Lime required:

$$\begin{array}{rcl}
 385 \text{ (Calcium bicarbonate)} \times .346 \times .00833 & = & 1.11 \\
 143 \text{ (Magnesium sulphate)} \times .466 \times .00833 & = & .57 \\
 \hline
 & & 1.68 \text{ pounds of pure lump lime per 1000 gallons.}
 \end{array}$$

If only 90 per cent efficient, which is the usual strength calculated for water softening plants, the real amount needed would be 1.68 divided by .90=1.86 pounds of 90 per cent lump lime per 1000 gallons. This value checks with the amount calculated above from the analysis by ions.

Soda ash required:

(Magnesium sulphate requires both lime and soda ash and calcium sulphate soda ash alone.)

$$143 \text{ (Magnesium sulphate)} \times .881 \times .00833 = 1.05$$

$$119 \text{ (Calcium Sulphate)} \times .779 \times .00833 = .77$$

1.82 pounds per 1000
gallons of pure so-
dium carbonate.

If 95 per cent efficient (the usual value for such calculations) the real amount would be 1.82 divided by .95=1.92 pounds of 95 per cent soda ash per 1000 gallons. This value checks fairly closely with the one obtained by the first method.

TABLE OF FACTORS FOR USE WITH HYPOTHETICAL COMBINATIONS

(Multiply the amount of the salt by the factor to obtain the chemical necessary to remove this salt as a scaling constituent. If the analysis is in parts per million, multiply the result by .00833 to obtain pounds per thousand gallons. If it is in grains per U. S. gallon, divide the result by 7 to get pounds per thousand gallons.)

Lime Factors	Lump Lime CaO	Hydrated Lime Ca(OH) ₂
Sodium Carbonate ...	0.529	0.699
Magnesium Chloride..	0.589	0.778
Magnesium Sulphate..	0.466	0.616
Magnesium Bicarbonate	0.767	1.014
Magnesium Carbonate	1.330	1.757
Calcium Bicarbonate..	0.346	0.457
Calcium Carbonate...	0.560	0.740
Soda Ash Factors:	Soda Ash (Na ₂ CO ₃)	
Calcium Chloride	0.955	
Magnesium Chloride	1.113	
Magnesium Sulphate	0.881	
Calcium Sulphate	0.779	

VARIATIONS IN COST OF CHEMICALS

The cost of chemicals varies according to the amount of hardness in the water, and the nature of the hardness. Two or three tenths of a cent per thousand gallons will cover the cost for a water that is so low in incrusting solids that it is a matter of doubt whether or not it should have outside treatment. As much as thirty cents per thousand gallons will be required to buy the chemicals for softening water that is so heavy in scaling constituents that it is hardly fit to use even when softened, due to the large amount of alkalies left in the water. It is, of course, true that the more expensive the treatment of a water, the more expensive it is to operate a power plant without treating the water. So where it is impossible to change the source of water, it is not a question of high cost of chemicals as much as it is the much higher cost of repairs, cleaning of boilers, and extra fuel used to heat through scale.

HOT PROCESS SOFTENER AS A PREHEATER

In calculating costs of chemicals on various types of softeners, it is necessary to take into consideration the fact that one kind of softener, namely the hot, continuous, lime-soda process combines in one the chemical treatment and the preheating of the boiler feed water. Thus the original cost of a preheater should be deducted from the cost of installing such a softener, and the lessened fuel cost due to a preheater should be charged off the cost of chemicals. With a well insulated hot process softener, it is estimated, that in the same way as a preheater, there is a saving of one per cent of fuel for each six degrees Centigrade or eleven degrees Fahrenheit. The saving thus amounts to 10 per cent and sometimes as high as 15 per cent of fuel.

4. Method of Control of an Intermittent Lime-Soda Softener

Every manufacturer of a standard water softening system furnishes along with the apparatus full details for its control and operation. Hence no attempt will be made here to go into these questions for any other kind than a home-constructed intermittent tank softener. The details of the chemical control of

practically all lime soda softeners are practically the same. As stated before, the only control used with a Permutit system is the soap test for hardness.

NECESSITY FOR CHEMICAL CONTROL

In the first place, it must be emphasized that a rigid control is absolutely necessary in the operation of any sort of softening plant, and this is particularly true with as crude an apparatus as a home-constructed tank softener must necessarily be. No engineer would think of operating a steam boiler without accurate steam gauges. The immediate consequences of lack of control of a softening system are not so serious as disregard of steam pressure, but they are sufficiently expensive. The failure of most water softening systems to deliver a satisfactory quality of boiler feed water may be laid to loose and careless methods of control. The control is so simple that any ordinary fireman can operate it if he is faithful and conscientious. About the only thing that can disqualify a man of ordinary intelligence from handling the chemical control on a water softener is color blindness. It certainly requires no knowledge of chemistry.

HOW TO FIX FEED OF CHEMICALS TO MEET VARIATIONS IN WATER

An analysis of the water is necessary in order to fix the initial feed of chemicals when the plant operation is first begun. Details of the method of calculation from the analysis have already been given. Once the analysis has been obtained from a chemist, it is possible to provide for fluctuations in the dissolved solids in the water due to seasonal changes.

USE OF ONE CONSTITUENT TO FIX AMOUNT OF CHEMICALS

It is usually safe to assume all of the constituents will vary in about the same amount as one individual constituent. The easiest one to determine is the bicarbonate ion, the amount of which is tested for by the addition of an acid solution of known strength to a measured amount of the water. For instance, according to the analysis given above the amount of the bicarbonate ion is 290 parts per million. From the whole analysis it was calculated that this water required 1.86 pounds of 90 per

cent lump lime and 2.10 pounds 95 per cent soda ash to every 1000 gallons of raw water. A change in the amount of this ion will call for a proportionate increase or decrease in both lime and soda. As will be shown later, when an acid of definite strength, known as "fiftieth normal" is used, each cubic centimeter (measured in an ordinary burette such as is used in any chemical laboratory) equals about 24 parts per million of bicarbonate ion when a 50 cubic centimeter sample of the water is used. The burette reading in the case just cited is about 12 cubic centimeters of acid. If a water requiring that amount of acid for a fifty cubic centimeter sample calls for 1.86 pounds lump lime and 2.10 pounds soda ash per 1000 gallons, it is reasonable to infer that if all constituents change as do the bicarbonates: when 13 cubic centimeters are needed, the chemical feed must be increased by one-twelfth. For by simple proportion, 12 is to 13 as 1.86 is to 2.02: and 12 is to 13 as 2.10 is to 2.28. Hence the lime feed will be increased to 2.02 pounds and the soda ash feed to 2.12 pounds per thousand gallons. From this it is easy to see how a table may be constructed that would provide for all changes due to variations in the amount of the dissolved solids in the water.

PREPARATION OF A TABLE FOR AMOUNT OF CHEMICALS

The rule for making a table like this is relatively simple. Calculate from the analysis the amount of lime and soda ash necessary from the formulas of Stabler, or take the value given by the chemist who has made the analysis. Divide by 24 the amount of bicarbonates reported as parts per million in the analysis of the water to be softened. Put down these three values thus:

Bicarbonates divided by 24. Lime Required. Soda Required. Take values varying from 4 above to 4 below the value obtained by the division of the bicarbonates by 24 and calculate by simple proportion the amount of lime and soda corresponding to these values, as was just done in the foregoing paragraph. In the case of the example already cited, the entire table would be as follows:

Number of Cubic Centimeters of N/50 Acid (Bicarbonates divided by 24)	Amount of Lump Lime (90%) Required for 1000 gallons	Amount of Soda Ash (95%) Required for 1000 gallons
8	1.24	1.40
9	1.39	1.57
10	1.55	1.75
11	1.71	1.92
12	1.86	2.10
13	2.02	2.28
14	2.17	2.45
15	2.32	2.62
16	2.48	2.80

HOW TO DETERMINE BICARBONATES

The details of the chemical tests to determine the amount of bicarbonates are these: Measure out 50 cubic centimeters of the raw water (filtered if muddy) into a porcelain dish. Add three drops of methyl orange indicator. (This is an organic dye that shows whether a solution is acid or alkaline.) The water will be colored yellow if there are any bicarbonates present. Run in fiftieth normal acid solution from a burette, stirring the water with a glass rod, until the color changes from yellow to a distinct pink. The difference between the reading of the acid levels in the burette before and after the test is recorded and is called the bicarbonate reading.

APPARATUS AND SUPPLIES FOR TESTING WATER

Following is the equipment necessary for the testing of water at a softening plant:

Acid Solution. Fiftieth normal (N/50) acid potassium sulphate (KHSO_4). Five liter lots.

Soap Solution. Alcohol (grain, not denatured) and water, 3:1, solution of castile soap of such strength that each cubic centimeter is equivalent to a milligram of calcium carbonate, made up according to Mason's Examination of Water; two liter lots.

Methyl orange indicator, water solution, one gram to one liter.

Phenolphthalein indicator, ten grams to one liter of 50 per cent alcohol (grain, not denatured).

Two 50 cubic centimeter Shellbach burettes with glass stop cocks, 1/10 cc. divisions.

Two porcelain evaporating dishes, shallow form, 6 inches in diameter, inside glaze.

Two dropping bottles, preferably with glass stopper and grooved pouring point on stopper.

One measuring cylinder of 100 cubic centimeters capacity, 1 cc. divisions.

One 250 cubic centimeter glass stoppered bottle for hardness test with soap solution.

Half dozen stirring rods of glass with rounded ends, about half the thickness of a lead pencil.

Half dozen gallon glass bottles with cork stoppers with handle. (Get at any drug store.)

One burette stand for holding two burettes.

Half dozen 250 cubic centimeter, low form, Griffin model. lipped beakers.

Two 3 inch glass funnels.

5. Operating a Home-Constructed Softener

WEIGHING OUT CORRECT AMOUNT OF CHEMICALS

Look up in the table the amount of lime and soda ash called for by this bicarbonate reading, and weigh out the correct amount for the number of gallons to be treated. Assume that the burette reading on the water given above was 12 cubic centimeters and the tank has a capacity of 10,000 gallons. The amount of lime would be 18.6 pounds and the soda ash 21.0 pounds.

PREPARING CHEMICALS FOR USE

Slake the required amount of lime, if lump lime is used, with the least amount of water necessary to change it to hydrated lime. (A good grade of lime will slake smoothly without lumps. If lumps of unburned material are found they should be gotten out and their amount allowed for in calculating the lime dosage.) Put it into the lime barrel and fill this with water. In the softener designed above, the lump lime is to be slaked and made into milk-of-lime in the barrel by running steam into the lime

barrel after the lime charge has been put in and covered with water. Put the required amount of soda ash into the other barrel and allow it to dissolve. This salt goes into solution very readily.

TREATING THE WATER

Fill the tank about two-thirds full. Add all of the prepared chemicals at this time. Turn on the stirrers and finish filling the tank. It is always best to add the entire amount of the chemicals to a part of the water and then complete the filling than to fill first and then add the chemicals. The reactions start more readily with an excess of the chemicals and the sludge is coarser. Keep the lime suspension well stirred and flush out the barrel with a hose so as to get all the lime into the softening tank. Let the stirrers run an hour in the full tank. Cut off the stirrers and allow the contents of the tank to stand three hours unstirred. By this time the sludge will have settled out enough so that the tank may be emptied through a filter into the storage tank.

VALUE OF OLD SLUDGE

It is not necessary to draw off the sludge after each run. In fact it is a decided advantage always to have some old sludge present. The very fine precipitates first formed will grow on the larger particles of the old sludge, and hence settling and clearing is quicker.

SUMMARY OF MOST IMPORTANT FEATURES

The points to be observed in the actual operation of the softener are these:

Employ the correct amount of chemicals.

See that the lime suspension is well stirred and that no lime is left in the lime barrel.

Add the chemicals before the tank is more than two-thirds full. Stir thoroughly and never less than one hour. (Practical experience has shown that a tank stirred only by the swirling motion of the inflowing water requires as much as twenty hours to clear, while the same tank with thorough stirring clears in four hours. Stirring increases the capacity of the softener four or five times, and relieves the filter.)

Always leave some old sludge in the tank.

Never operate a home-constructed softener without a good sand or quartz filter.

6. Testing the Treated Water

REASONS FOR TESTING

Every tank of water should be tested to see if the treatment was correct. In the first place, it is possible from these results in a short time to correct the table of chemicals needed for each bicarbonate reading to conform still more closely to the actual conditions of the water and the softener. A control is necessary to correct any defects in treatment due to wrong weights of chemicals or to the use of chemicals not up to standard efficiency. After all it is this final test of the treated water that is most important. These tests should always be made before the softener is emptied, so that any mistakes may be corrected by adding more chemicals or more raw water according to the indications of the tests.

DETAILS OF TESTING TREATED WATER

Following are the details of the three tests designated as "P", "M", and "H".

P

To 100 cubic centimeters of the water measured into a clean porcelain dish, add five drops of phenolphthalein indicator. This will give the solution a purplish red color. While stirring the mixture, run in N/50 acid until the solution has just lost its color. Record this amount of acid as "P".

M

To the same water sample after the first test has been made, add three drops of methyl orange solution and while stirring the mixture continue to run in acid until the yellow color changes to a faint red. Read off the total amount of acid used, which includes the amount recorded as "P" and call the total reading "M".

II

Put 100 cubic centimeters of the treated water in a 250 cubic centimeter capacity glass stoppered bottle. Run in standard soap solution a few drops at a time and shaking the bottle hard between each addition. At first the lather will disappear instantly, but as more soap solution is added, the bubbles become tougher and persist longer. At a point where the magnesium salts have all been used up to form the insoluble compound between the acids of the soap and the magnesium, the bubbles, though small, will persist for as much as a minute. This is not an end point. Continue to add soap solution and shake, and as long as there is any calcium radicle present the lather will disappear. When the correct end point is reached, there will be a rich lather, which will stand for several minutes. The least amount of soap solution which gives this result should be recorded as a measure of the hardness of the water as "H."

WHAT THE RESULTS MEAN

From these results it can be determined whether or not the water has been correctly treated.

1. Soda Ash. In a properly treated water one-half of the M reading should be equal to some value which is not less than the H reading plus one nor more than the H reading plus three. If one-half M is less than H plus one, not enough soda ash has been added. If one-half M is greater than H plus three, there has been too much soda ash put in.

2. Lime. When water has been correctly treated with lime, the value for P should fall between one-half and three-fourths the value of M. If P is less than one-half M, there is not enough lime. If P is greater than three-fourths M, too much lime was used.

Following are practical examples:

1. P—7.9, M—12.5, H—4.9.

$\frac{1}{2}$ M—6.3, which is between H+1 (5.9) and H+3 (7.9). Soda ash correct.

P—7.9, which lies between $\frac{1}{2}$ M (6.3) and $\frac{3}{4}$ M (9.4). Lime correct.

2. P—5.3, M—15.2, H—7.5.

$\frac{1}{2}$ M—7.6, which is less than H+1(8.5). Not quite enough soda ash.

P—5.3, which is less than $\frac{1}{2}$ M(7.6). Not quite enough lime.

RECORDING RESULTS OF TEST

All tests, the amount of chemicals used and their cost, the amount of water softened, and the total cost for chemicals and labor should be recorded and kept. Following is a copy of a week's report furnished by the Austin Street Railway Company to the University Division of Chemistry. A report on the results of the softener used by this company is given in the next chapter.

SAMPLE REPORT Water Softening Report AUSTIN STREET RAILWAY COMPANY Week Ending March 3, 1917

The following is a copy of a Weekly Report furnished by the Austin Street Railway Company to the Division of Chemistry. It is given by way of suggesting a convenient form for recording results.

Water treated: 30,000 gallons. Labor 4 hours @ 15c.=60c.

Sunday: Raw water(50cc.) M 15.1; lime 38 lbs.; soda ash 28 lbs.
H+1=4.2 H+3=6.2 H+1=9.5 H+3=11.5

Tank 1. P 6.2, M 12.6, H 3.2; P 7.5, M 14.2, H 8.5. Labor \$.60
H+1=5.6 H+3=7.6 Chemicals 3.09

Tank 2. P 7.6, M 12.8, H 4.6; P—, M—, H—. Total \$3.69
114 lbs. lime @ $\frac{1}{2}$ c.=\$0.57.
84 lbs. soda ash @ 3c.=\$2.52

Water treated: 50,000 gallons. Labor 10 hours @ 15c.=\$1.50

Monday: Raw water(50cc.) M 15.1; lime 38 lbs.; soda ash 28 lbs.
H+1=7.4 H+3=9.4 Labor \$1.50

Tank 1. P 7.3, M 17.3, H 6.4; P—, M—, H. Chemicals 5.15
H+1=8.8 H+3=10.8

Total \$6.65

Tank 2. P 6.9, M 13.7, H 7.8; P—, M—, H—.
190 lbs. lime @ $\frac{1}{2}$ c.=\$0.95.
140 lbs. soda ash @ 3c.=\$4.20.

Water treated: 40,000 gallons. Labor 8 hours @ 15c.=\$1.20.

Tuesday: Raw water(50cc.) M 15.0; lime 38 lbs.; soda ash 28 lbs.
H+1=5.6 H+3=7.6 H+1=5.9 H+3=7.9. Labor \$1.20

Tank 1. P 7.5, M 13.9, H 4.6; P 6.4, M 10.9, H 4.9.
Chemicals 4.12
H+1=5.9 H+3=7.9 H+1=7.3 H+3=9.3

Total \$5.32

Tank 2. P 7.3, M 11.9, H 4.9; P 6.2, M 11.9, H 6.3
152 lbs. lime @ $\frac{1}{2}$ c.=\$0.76.
112 lbs. soda ash @ 3c.=\$3.36.

Boiler Waters

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Water treated: 40,000 gallons. Labor 8 hours @ 15c.= \$1.20.

Wednesday: Raw water (50cc.) M 14.7; lime 36 lbs.; soda ash 26 lbs.
 $H+1=10.8$ $H+3=12.8$ $H+1=10.8$ $H+3=12.8$

Labor \$1.20

Chemicals 3.84

Tank 1. P 6.4, M 19.0, H 9.8; P 5.6, M 15.4, H 9.8

Total \$5.04

$H+1=10.5$ $H+3=12.5$ $H+1=10.6$ $H+3=12.6$

Tank 2. P 4.5, M 17.4, H 9.5; P 3.7, M 12.4, H 9.6

144 lbs. lime @ $\frac{1}{2}$ c.= \$0.72.

104 lbs. soda ash @ 3c.= \$3.12.

Water treated: 30,000 gallons. Labor 4 hours @ 15c.= 60c.

Thursday: Raw water (50cc.) M 15.6; lime 38 lbs.; soda ash 28 lbs.
 $H+1=6.2$ $H+3=8.2$ $H+1=8.8$ $H+3=10.8$. Labor \$.60

Tank 1. P 6.1, M 10.4, H 5.2; P 6.1, M 13.2, H 7.8

Chemicals 3.09

$H+1=6.0$ $H+3=9.0$

Tank 2. P 6.7, M 9.7, H 5.0; P—, M—, H—.

Total \$3.69

114 lbs. lime @ $\frac{1}{2}$ c.= \$0.57.

84 lbs. soda ash @ 3c.= \$2.52.

Water treated: 30,000 gallons. Labor 4 hours @ 15c.= 60c.

Friday: Raw water (50cc.) M 15.0; lime 38 lbs.; soda ash 28 lbs.
 $H+1=4.6$ $H+3=6.6$ $H+1=4.1$ $H+3=6.1$. Labor \$.60

Tank 1. P 6.2, M 11.7, H 3.6; P 7.3, M 11.0, H 3.1

Chemicals 3.09

$H+1=6.5$ $H+3=8.5$

Tank 2. P 6.3, M 10.3, H 5.5; P—, M—, H—.

Total \$3.69

114 lbs. lime @ $\frac{1}{2}$ c.= \$0.57.

84 lbs. soda ash @ 3c.= \$2.52.

Water treated: 30,000 gallons. Labor 4 hours @ 15c.= 60c.

Saturday: Raw water (50cc.) M 15.0; lime 38 lbs.; soda ash 28 lbs.
 $H+1=3.3$ $H+3=5.3$ $H+1=4.6$ $H+3=6.6$. Labor \$.60

Tank 1. P 6.6, M 11.9, H 2.3; P 6.2, M 10.9, H 3.6

Chemicals 3.09

$H+1=4.4$ $H+3=6.4$

Tank 2. P 6.1, M 10.0, H 3.4; P—, M—, H—

Total \$3.69

114 lbs. lime @ $\frac{1}{2}$ c.= \$0.57.

84 lbs. soda ash @ 3c.= \$2.52.

REMARKS:

Total cost, chemicals and labor, water softening plant

for seven days \$31.77

Cost per K. W. hour..... .0007

Cost per 1000 gallons water..... .127

Water treated 250,000 gallons

(Signed)

W. T. READ,

Chemist.

H. D. ODELL,

Chief Engineer.

CHAPTER FOUR

RESULTS

“Does water softening pay?” It is the object of this chapter to prove that *water softening pays*. It pays not only in the increased ease and satisfaction in operating a steam power plant, but it pays big returns on the investment in dollars and cents, as shown in the annual reports of any company using softened water. The experience of a number of manufacturers are given, and one particular case which has been thoroughly studied by the Division of Chemistry is given in detail.

*1. Savings Effected by Water Softening Plants***GENERAL FACTS**

Before taking up specific instances, a few general facts will be given. The cost of turbinizing scaled water tubes has been given at a minimum of about $\frac{1}{2}$ c. per lineal foot and often runs as high as 2c per foot for each cleaning. Add to this the cost of fuel required to bring a cold boiler up to steaming after each shut-down for scale removal. It is estimated that it costs 10 pounds of coal for hand fired and 15 pounds of coal for stoker-fired furnaces per horse power to cool down a boiler for cleaning and to fire it up again for service. Thus a 600H.P. boiler turbinized once a month would cost from \$250 to \$500 annually for cleaning alone. All of this may be obviated by the use of a water softener.

Several years ago the American Railroad Association adopted as an official standard value *seven cents per pound of incrusting solids* removed from a scaling water as the *saving* effected by softening the water supply. Against this was charged the cost and maintenance of the softening plant, reducing the net saving to four cents per pound of scale removed. With present high prices of fuel and labor; it is safe to consider *ten cents* per pound of scale removed as a fair estimate of saving due to softening water. This means that if a water supply carried 4 pounds of scaling ingredients per 1000 gallons, the removal of this scale would be worth at least 40 cents to the efficiency of the plant.

It has been shown that the chemicals necessary to remove this much scale will cost a little more than 7 cents. Assume labor and overhead expenses, such as interest on investment and depreciation of softening plant, cost 7 cents more, which is a most liberal estimate. This gives a softening cost of 14 cents per 1000 gallons. The softening has thus saved 26 cents per thousand gallons of water evaporated. Even if we take the figure given by the American Railroad Association, the saving is 14 cents per pound of incrusting solids removed, or 100 per cent *profit on the cost of softening*.

One practical engineer has summed up the book-keeping on the cost and profit of a water softener thus:

“Charge the softening plant with:

- (1) Interest and depreciation on softening plant, 10 per cent.
- (2) Labor cost annually.
- (3) Chemical cost annually. (Actual cost.)

Credit the softening plant with:

- (1) Cost of turbinizing tubes, with untreated water.
- (2) Cost of tubes lost due to scale and corrosion, with untreated water.
- (3) Cost of shutting down for cleaning, with untreated water.
- (4) Cost of tube repairs, when untreated water is used.
- (5) Cost of boiler compounds used, with untreated water.
- (6) Difference in cost of coal between use of treated and untreated water.
- (7) Cost of repairing furnace settings, when untreated water was used.
- (8) Increase in horse power hours without increased investment.
- (9) If hot process softener is used, increased temperature of feed water.

SOME ACTUAL SAVING EXPERIENCES

An automobile manufacturer saved \$6,000 in one year, or twice the total cost of the softener. The water supply carried 540 parts per million scaling solids which were reduced to less than 20.

A marble company has reduced coal consumption 21 per cent by use of softened water, or a net saving of \$1,200 a year on fuel alone.

A crucible steel company using 3,000 rated H.P. and 100,000 gallons of water per day report this saving:

3,600 tons of coal per year.....	\$ 9,000
Wages of two men per year.....	900
300 tubes per year.....	1,500
	<hr/>
	\$11,400
Less cost of chemicals and labor.....	636
	<hr/>
	\$10,764

This is three times the original cost of the softener.

A yarn mill saves \$5,000 per year on a 900 H.P. plant, which is twice what the softener cost.

Following is the estimate of savings based on a 1,000 H.P. boiler installation using Lake Michigan water. (The amount of incrusting solids in this water is low in comparison with most hard waters in Texas.) This plant operates under 24 hours a day service, seven days in the week, at an average load of about 400 H. P. When untreated water is used the boiler tubes must be turbed every four weeks, else the tube loss is serious. Extra help must be employed, as the regular organization has no time for this work.

Operating cost of a standard hot-process softener would be:

6 per cent interest on a total investment of \$2,000.....	\$ 120.00
7 per cent depreciation on a total investment of \$2,000	140.00
Chemical cost	105.12
Labor, 2 hours per day (performed by regular force)...	219.00
	<hr/>
	\$ 584.12

Savings:

Boiler compound, \$20 per month.....	\$ 240.00
Savings due to continuously clean heat surface, 5 per cent on \$18,000 annual coal bill.....	900.00

Turbining 7,128 lineal feet 31½ inch tube at 1c per foot, 10 times per year.....	712.80
1,500 tube gaskets per year saved.....	240.00
Heat loss in cooling down and reheating boiler 10 times per year, 50 tons at \$2.40 per ton.....	120.00
	<hr/>
	\$2,212.80
Saving per year.....	\$1,628.68

These examples given above have been taken at random from the experineces of average plants using average hard water.

2. *Austin Street Railway Company Softener*

Thousands of instances might be accumulated as proof of the value of softening water. Yet, one instance which is a matter of absolute personal knowledge has done more to impress upon the chemists of the University of Texas the advantage of treating water to remove scaling constituents than all of the published records of distant manufacturers.

NATURE OF PLANT AND CONDITIONS AT BEGINNING OF EXPERIMENTS

In the summer of 1916, the University Division of Chemistry took up the study of water softening, using the plant of the Austin Street Railway Company for experimentation. The plant was home-constructed, and had all the faults of such systems. It consists of two 10,000 gallon cypress tanks on a platform, with barrels for chemical solutions and the usual arrangement of sludge and drain pipes. There is a large cooling pond for the turbine exhaust, which serves as a storage tank. The most glaring defect of the plant was the utter lack of stirring devices. The swirling motion imparted to the raw water as it was fed into the tank and mixed with the chemicals had been considered to be adequate agitation. As a result the plant was operating in a very inefficient and unsatisfactory manner. It required 20 hours to settle and clear each tank of water. Since an average of 30,000 gallons of water were needed for a day's run, it was necessary to use as much as 10,000 gallons of raw water. As it

happened, incorrect amounts of chemicals were being used, the water being badly overtreated with soda ash. So the amount of raw water about compensated for the excess of chemicals, and a fair degree of softening was obtained. There was no chemical

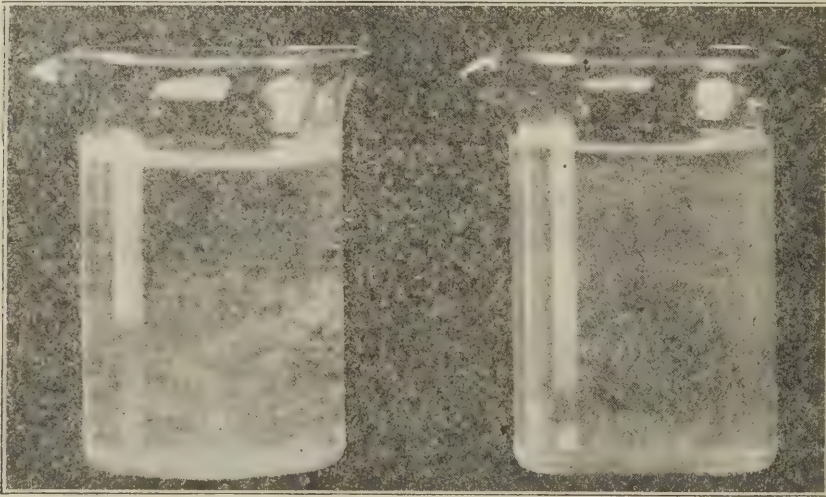


Fig. 16. Effect of stirring on precipitation. One minute after addition of chemical to water: "a" stirred, "b" unstirred.

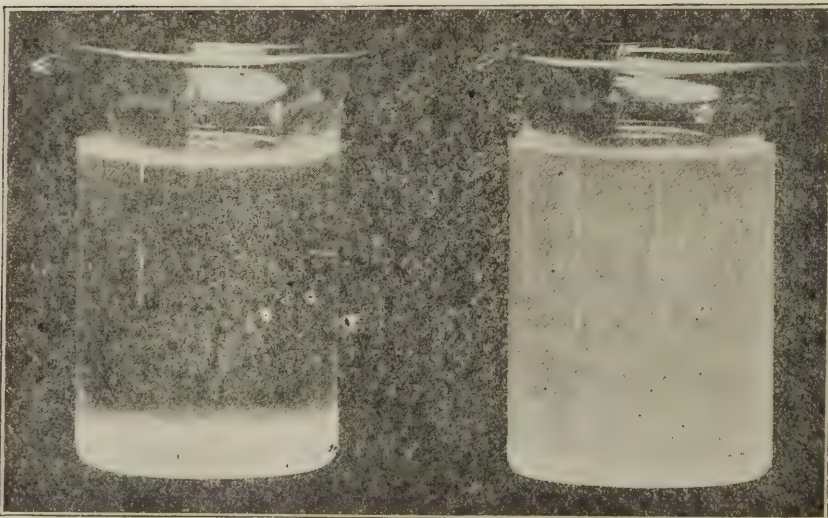


Fig. 17. Effect of stirring on precipitation. Five minutes after addition of chemical to water: "a" stirred, "b" unstirred.

control and the whole treatment was somewhat of the hit-or-miss variety that is so often the case when a chemical process is carried on without some preliminary chemical advice and adjustment. The president and engineer of the company were thoroughly open to advice and willing and anxious to cooperate fully in correcting defects.

CHANGES MADE

The first thing done was to change the feed of chemicals, and the next thing was to install adequate stirrers. A small motor-driven rotary air compressor was available, and an air line was put in to the tanks, and stirring carried out as described in Chapter III. The immediate result was that the tanks that had taken 20 hours to settle, cleared in 4 hours. As much as 50,000 gallons of treated water have been gotten from this softener in a day's run, and 60,000 gallons could have been gotten just as easily in the same time.

NATURE OF THE RAW AND TREATED WATER

When the work was first begun, and for several months afterward, the water was very hard and high in permanent hardness. An analysis made at the beginning of the experiments gave the following values:

	Parts per Million
Calcium	169
Magnesium	50
Sodium	180
Sulphates	276
Bicarbonates	437
Chlorides	264

Iron, aluminum and silica were present in negligible amounts. According to the Stabler formula this water will give 4.85 pounds of scale per 1000 gallons, with a hardness coefficient of 77 per cent. Some months later, due to emptying Lake Austin, the amount of dissolved solids dropped to nearly one-half its former value, which made softening much less of a problem.

The water supply is a shallow well, some four hundred yards from the Colorado River. It was dug with the expectation of getting the water that fills all the sands near the river. For

some time, about the same kind of water was obtained as that of the river. When the Austin dam was completed, and Lake Austin, which lies some two miles up the river, was filled, the quality of the water suddenly changed. The dissolved solids more than doubled, and there was a big increase in the relative sulphate content. It seems that the pressure of the water in the lake, there being about a sixty foot head, forced water through veins and strata which were impregnated with gypsum as well as through a limestone formation. During the summer of 1917, in order to furnish the rice growers of South Texas with adequate water supply, the lake was gradually drained. Within a few days, the quality of water in the street railway company's well improved and resembled the river water once more.

Samples of the treated water, taken on various occasions, showed from 6 to 14 parts per million of calcium and an average of 10 parts per million of magnesium. This is about the limit of efficiency of a cold-process lime-soda softener, that is from 35 to 70 parts per million of incrusting solids remaining in the water. Since there was always a slight excess of soda ash used, the remaining hardness did not form a scale, but produced a slight sludge in the boiler.

METHOD OF OPERATING SOFTENER

The details of chemical control, calculations of chemicals necessary by the method of variation of bicarbonates, testing of treated water, and the actual operation of the softener were all carried out as described in Chapter III.

FOAMING

When the water had been softened without chemical control, it was often the case that an abnormal excess of soda ash was used. As a result large amounts of sludge were produced in the boilers, and there was violent foaming. Even after correct treatment a great deal of foaming was experienced. With a view of getting at the cause of this trouble, samples of water were taken at the water line from the gauge cocks and the following analytical results obtained:

	1	2	3
Suspended Solids	1,188	492	2,016
Collodial Matter:			
(a) Ferric Oxide	31	43	7
(b) Alumina	5	32	11
Total Dissolved Solids	21,269	26,447	35,971
Ions			
Calcium	68	52	45
Magnesium	10	8	19
Sodium (by difference)	7,520	9,596	12,627
Carbonates	104	138	188
Bicarbonates	29	None	None
Chlorides	7,168	9,314	12,018
Sulphates	5,987	7,308	9,884
Hydroxyl	None	8	18

These results show not only an abnormally high concentration of alkali salts, but an excessive amount of suspended solids. The suspended matter obtained in these analyses proved to be largely silica, ferric oxide, alumina, calcium and magnesium salts, and some adsorbed alkalies. There were no carbonates at all in the suspended material. It was extremely finely divided, in fact was as fine as flour.

Without altering the chemical feed or any other factors in the operation of the softener, regular blowing down was advised. By blowing down several inches each night after the turbine was shut off, the foaming was stopped and has not since occurred to any serious extent.

While the concentrations of the boiler water in these cases are very high, the amount of sodium carbonate in this concentrated water is by no means as much as in many artesian waters that cause no trouble from foaming. It seems evident that the principal cause of foaming here was the suspended matter.

COST AND SAVINGS DUE TO WATER SOFTENING

Through the courtesy of Mr. W. J. Jones, president of the company, the following cost figures were made available:

Boiler Room Expenses:

	One Year with Untreated Water	One Year with Treated Water
Total Fuel and Water.....	\$23,894.03	\$22,017.96
*Labor (aside from regular firemen)....	2,746.26	2,578.59
**Cost of Chemicals	10.72	923.00
Net Saving of Second Year over First.....		\$1,131.45
Cost of Softener.....		621.72
Per cent Profit on Investment in one year's operation....		182%

AVERAGE COST OF OPERATION

Following is a summary of a week's run for the week ending April 28, 1917:

Water treated	210,000 gallons
Labor 28 hours at 15c.....	\$ 4.20
Lime 756 lbs. at ½c.....	3.78
Soda 564 lbs. at 3c.....	16.92
<hr/>	
Total cost	\$24.90
Cost per K. W. hour.....	\$0.0005
Cost per 1000 gallons.....	.118

(During the past summer, the cost has dropped, owing to the change in the water, to about 8c per 1000 gallons.)

The most interesting things about the experiment are the results obtained in smooth operation of the plant and greatly reduced cost of maintenance. When the raw water was being used, four laborers were continually employed cutting scale from one set of boilers while the other set was steaming. In reply to a question as to how often each boiler was cleaned, one of the firemen of the plant replied "Just as fast as we could get to them." As soon as one boiler was cleaned and filled for use, another was shut down and opened up for cleaning. One boiler kept in service less than two months, while untreated water was being used, required three full weeks for cleaning, with two turbines running all day, and two men going after the scale with chisels. Four barrow loads of scale came out of the boiler, and it was extremely hard scale. The same boiler was operated a full year with treated water. During this time, there was

*This includes in the first year the cost of cleaning boilers, in the second not only handling softener, but various changes and improvements in boiler room, for which under old conditions men had no time.

**First year covers boiler compounds used occasionally, second year lime and soda ash.

quite an interval when the softener was operated without control, sometimes only partly treated water being fed, and at intervals raw water going in. Even under these unsatisfactory conditions, when the boiler was opened up after a year's solid service, it was cleaned in *four hours* easy work, and about half a barrow of scale, mostly sludge was gotten out. Put the two up against each other: two months run, three weeks hard work to clean, four barrows of scale; six times the length of run, one-fiftieth the labor, one-eighth the scale.

Where tube trouble was a continuous thing under old conditions, sometimes as many as seven going out in a day's run, when the load hovered around the peak all day, now tube trouble is unknown.

A boiler inspector for this district, who has five hundred boilers under his care, has ranked the boilers of the Austin Street Railway Company as among the best half dozen in point of condition of his entire five hundred.

SUMMARY

From the above figures it will be seen that this company paid for the softener in one year and cleared \$450 besides. Charging the softener with 10 per cent to cover depreciation and interest on the investment, a yearly charge of about \$65 is balanced against a yearly net saving of \$1,100, which is a fair profit. \$1,000 per year may look like a high chemical bill, but this firm pays this bill and clears more than \$1,000 besides as compared with the cost of operation with untreated water. These results were gotten with the crudest and least efficient and most expensive (in point of operation cost) of all types of softeners. It is true that the plant had the care and attention of a chemist for some time; but the chemist had to learn first the practical details of water softening. This experience is available to the public in the pages of this bulletin. By an intelligent reading of what is given here, by faithfully following directions, supplemented by answers to specific questions suggested by individual difficulties, any engineer ought to be able to operate a water softener successfully.

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